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The experimental observation, mechanism and kinetic studies on the reaction of hexachloro-1,3-butadiene initiated by typical atmospheric oxidants

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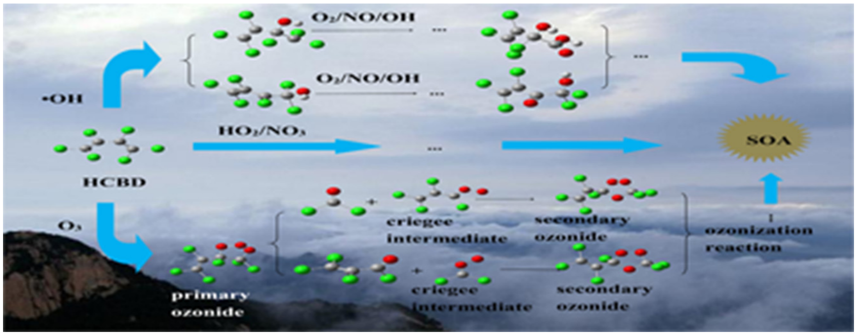
HIGHLIGHTS

- The concentrations of HCBD in landfills and high altitude of mountain are more than in other observation places.
- Hexachloro-1,3-butadiene initiated by typical atmospheric oxidants can lead to different mechanism.
- The total rate constants of the Cl, NO_3, HO_2, OH and O_3 with HCBD at 298.15 K is 4.51×10^{-13} cm^3 $molecule^{-1}$ s^{-1}.
- The ratio of OH and Cl radicals with HCBD are more than those of NO_3, HO_2 and O_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexachloro-1,3-butadiene (HCBD) is a persistent organic pollutant in the environment. When its samples were collected and observed, the levels of HCBD in its source and high mountains are higher than in urban cities, oil factories and countryside. The density functional theory is applied to the degradation mechanism of HCBD with Cl, NO_3, HO_2, OH and O_3. Those reactions are optimized and calculated at two carbon sites of double bonds, and then the subsequent reactions of the OH-initiated intermediates with O_2 and NO are taken as examples. Ozonization reactions of HCBD including the formation of primary and secondary ozonides are investigated. The Criegee intermediates created in the ozonization reactions can react with O_2, SO_2, NO_2 and H_2O. Reaction rate constants of the Cl, NO_3, HO_2, OH and O_3 initiated reactions with HCBD are calculated within 200 to 400 K with the transition state theory method, and the rate constants of the Cl, NO_3, HO_2, OH and O_3 at 298.15 K are 4.51×10^{-13}, 1.32×10^{-20}, 4.33×10^{-29}, 6.33×10^{-16}, 5.80×10^{-27} cm^3 $molecule^{-1}$ s^{-1}, respectively. The reactions of OH and Cl radicals with HCBD are more important than those of NO_3, HO_2 and O_3 according to the reaction rate branching ratio. Both the temperature and reaction rate could change with the height.

1. Introduction

Although hexachloro-1,3-butadiene (HCBD) is a persistent organic pollutant (POPs), it is still widely used for intermediates, transformer, hydraulic or heat transfer liquids in chemical production and pesticides.

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In addition, it could still be unintentionally released as byproducts in the manufacturing of chlorinated hydrocarbons (Lecloux, 2004). This kind of halohydrocarbon has volatility and a long half-life in atmosphere and water. It will reassign into the atmosphere when released into water and soil, and stay in the atmosphere when discharged into air (Vorkamp and Rigét, 2014). HCDB may stay in air until it contacts with OH radical or is photochemically degraded, deposited and biodegraded in water or soil sediments (Constant et al., 1995; Cord-Ruwisch et al., 2009). As for aquatic organisms, the HCBD is bioaccumulative, carcinogenic and toxic (Lecloux, 2004).

There is no natural source for HCBD (UNEP, 2012), but it can be discovered in both living and non-living things (Taylor et al., 2003). Based on air samples and model tests, the global budget for HCBD was estimated at 3 k tons/year (Class and Ballschmiter, 1987). According to the emission inventory of POPs made by United Nations Economic Commission for Europe (UN-ECE), 2.59 tons of HCBD was discharged to the environment in 2000 (van der Gon et al., 2007). Though HCBD was forbidden to produce in the UN-ECE region, USA and Canada, a complete ban on industrial HCBD emission is unachievable for it could get into atmosphere as byproducts (Mumma and Lawless, 1975). Around the industrialized areas, the underground water could be contaminated by HCBD (Fattore et al., 1998), and even fish in polluted rivers were detected to carry HCBD (Jürgens et al., 2013; Macgregor et al., 2010). Of course the surrounding soil and terrestrial organisms could also be polluted (Tang et al., 2014; Zhang et al., 2014). The volatile organic compounds in contaminated rivers can evaporate and are harmful to nearby creatures (Barnes et al., 2002; Juang et al., 2009). Besides, in sediments samples from estuaries and coastal areas, HCBD can be detected too (Lee and Fang, 1997; Lee et al., 2000).

There have been numerous studies on the degradation of HCBD. On the basis of the rate constant for vapour phase reaction of HCBD with OH radical, its half-life in air is reported to be about 0.3–3.3 years (Mackay et al., 2006). HCBD can be removed from aqueous solution by solvent sublation and air stripping (Shih et al., 1990). Based on ozonization, adsorptive ozonization and ozone combined with zero-valent iron nanoparticles, the HCBD and other organochlorine pesticides can be removed from water. And the use of O_3/UV process is more efficient (Derco et al., 2015). The pyrolysis processes of HCBD were also reported, the thermal degradation in the liquid phase are studied at 120–210 °C and the products have been detected (Ageev and VA, 1968). Moreover, in the gas phase, the reactions are at 500–1000 °C and the intermediates and final products are identified by Gas Chromatography-Mass Spectrometer (GC/MS) (Baillet et al., 1996). HCBD in soil is able to be oxidated and removed with the in situ chemical oxidation technique (de Weert et al., 2014). Besides, in vadose zone soil or sediments, the biodegradation processes of HCBD like the reductive dechlorination are also viable (Cord-Ruwisch et al., 2009; Yee et al., 2010).

Recent studies focus on collecting the environmental samples (Dsikowitzky et al., 2004) for the HCBD detection and performing experiments (Li et al., 2008) about the HCBD degradation. The quantum calculation can be used to find the specific reaction processes and energy changes. In this study, the sample collection, analysis and quantum method are combined to reflect the distribution rule and the degradation reaction mechanism. The reactions of HCBD with Cl, NO_3, HO_2, OH radical and O_3 are performed, and the results are used to calculate rate constants at the temperature ranging from 200 to 400 K. Meanwhile, the relationship between temperature and rate constants should fit the Arrhenius formulas (Laidler, 1984). The reactions that OH radical and O_3 react with HCBD are taken as an example for the subsequent reactions.

2. Methods

2.1. Sampling and analyses

The air samples were collected from Mount Tai (1534 m), refuse landfills, urban areas, countryside and oil factories from April to June in 2017. Sampling and analyses in this research referred to method Environmental Protection Agency (USEPA) TO-14 (Agency, 1999a) and TO-15 (Agency, 1999b). The ambient air samples were collected in fused silica-lined stainless steel vacuum canisters (SUMMA, 3.2 L). The canisters were evacuated to <100 mTorr and pressurized to 20 psi with humid nitrogen before sampling collection in three cycles, using a Canister Cleaner 3100 to remove compounds. The canisters were finally analyzed in the laboratory within 30 days.

The air samples were pre-concentrated using an Entech7100 pre-concentrator and then analyzed using a GC–MS system (Agilent7890B-5977A) on an internal standard method. The air samples were mixed at internal standards and pumped into the pre-concentrator with a three-stage cryotrap (Module 1–3). Firstly, the air samples were concentrated in a glass bead trap whose temperature was maintained at −150 °C with liquid nitrogen (module 1). And then the samples were recovered at 10 °C via desorbing. This step is to leave most of the liquid water behind in the first trap. The trapped analytes were subsequently baked at 150 °C for 5 min to be transfererd to module 2. The second cryotrap was maintained at −30 °C and permitted the trapped compounds to pass through and would leave the carbon dioxide behind. Then the concentrated components were again desorbed at 180 °C for 2.5 min and subsequently they concentrated at the cold top of the capillary column in Module 3, which was cooled to −160 °C. Finally, the highly concentrated compounds were rapidly desorbed at 180 °C and swept into the column for separation and analyses. Helium (99.999%) was used as the purge gas for the cryogenic pre-concentrator and carrier gas for the GC. As many as 65 compounds were measured in this progress and HCBD was analyzed in this paper.

The internal standard 3-bromofluorobenzene was used for HCBD quantification and added to each sample before analyses in order to trace the analytical procedure. HCBD was identified according to its retention time and m/z based on USEPA standard gases and the analysis was conducted under the SIM (selected ion monitoring) mode and quantified using the internal standard method with multi-point standard curves. The correlation coefficient of the curve was 0.997, demonstrating that the integrated areas of peaks were proportional to the concentrated HCBD.

2.2. Mechanism study

All work is implemented in the Gaussian 09 programs package, and density functional theory (DFT) (Zhao and Truhlar, 2005) has been applied to quantum chemistry calculation. The density functional theory is a promising and useful calculation tool which is widely used in quantum calculation of chemistry reactions (Zhao and Truhlar, 2004). In this study, the geometries of the reactants, transition states, intermediates, complexes and products are all optimized with MPWB1K method (Mazarei and Mousavipour, 2017; Slanina et al., 2008) at the 6–31 + G (d,p) level. The corresponding vibrational frequency calculations are kept at the same level and the results are used to determine the attribute of stationary points. The transition states are confirmed by the intrinsic reaction coordinate (IRC) analysis whether they connect the designated reactants and products. The single point energy calculations for the stationary points are carried out at the 6–311 + G (3df,2p) level (Qu et al., 2017).

2.3. Kinetic calculation

The transition state theory (TST) is used to calculate the reaction rate constants, with the temperature ranging from 200 to 400 K. The IRC analysis is used in kinetic calculation and all results of rate constants with temperature should fit the Arrhenius formulas. Meanwhile, the correlative R^2 is given.