



Atmospheric oxidation of hexachlorobenzene: New global source of pentachlorophenol



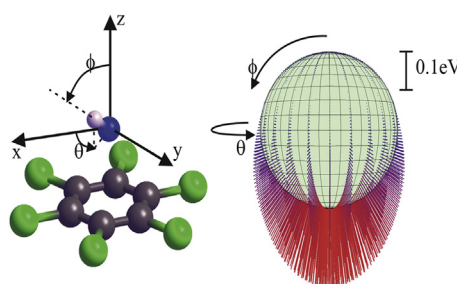
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HIGHLIGHTS

- We explored the reaction mechanism of atmospheric oxidation of hexachlorobenzene.
- The addition of OH radical to hexachlorobenzene proceeds via pre-reaction complex.
- In prereaction complex oxygen atom is pointing to the center of aromatic ring.
- Reaction rates are determined for the whole range of environmental temperatures.
- Pentachlorophenol is stable product in atmospheric oxidation of hexachlorobenzene.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexachlorobenzene is highly persistent, bioaccumulative, toxic and globally distributed, a model persistent organic pollutant. The major atmospheric removal process for hexachlorobenzene is its oxidation by hydroxyl radicals. Unfortunately, there is no information on the reaction mechanism of this important atmospheric process and the respective degradation rates were measured in a narrow temperature range not of environmental relevance. Thus, the geometries and energies of all stationary points significant for the atmospheric oxidation of hexachlorobenzene are optimized using MP2/6-311G(d,p) method. Furthermore, the single point energies were calculated with G3 method on the optimized minima and transition-states. It was demonstrated for the first time that the addition of hydroxyl radicals to hexachlorobenzene proceeds indirectly, via a prereaction complex. In the prereaction complex the hydroxyl radical is almost perpendicular to the aromatic ring while oxygen is pointing to its center. In contrast, in the transition state it is nearly parallel with the aromatic ring. The reliable rate constants are calculated for the first time for the atmospheric oxidation of hexachlorobenzene for all environmentally relevant temperatures. It was also demonstrated for the first time that pentachlorophenol is the major stable product in the addition of hydroxyl radicals to hexachlorobenzene and that atmosphere seems to be a new global secondary source of pentachlorophenol.

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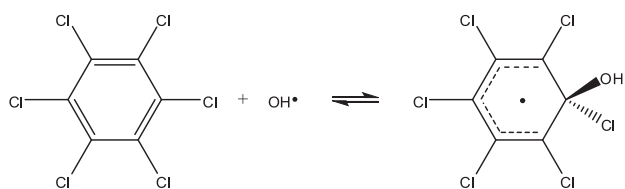
1. Introduction

Hexachlorobenzene (HCB) is one of the twelve major persistent organic pollutants (POPs) listed under the Stockholm Convention

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(Wania and Mackay, 1996). It is highly persistent, bioaccumulative, toxic and globally distributed (Sabljic, 2001; Shen and Wania, 2005) and as such it is a model persistent pollutant. Due to its semi-volatile nature, HCB can easily undergo atmospheric long-range transport by the repeated air-surface exchange or “hopping” and today it is regularly detected all over the world in the air, soil, water, sediment, biota and human tissues including the remote areas, i.e. the arctic region and the Antarctic, far away from its primary sources (Barber et al., 2005; Choi and Wania, 2011; Galban-Malagon et al., 2013a, 2013b). For example, in the recent study on the levels of POPs in the US population HCB was detected in 99.9% of human serum samples of the persons age 12 or older (Patterson et al., 2009). HCB is considered a probable human carcinogen and is toxic by all routes of exposures (<http://www.epa.gov/iris/subst/>



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0374.htm). Short-term high exposures can lead to the kidney and liver damage, central nervous system excitation and seizures, circulatory collapse, and respiratory depression (<http://www.epa.gov/publ/pubs/hexa.htm>).

The global production of HCB peaked in the late 1970s and early 1980s with an annual production of 10,000 tons (Barber et al., 2005). Due to the world-wide restrictions on HCB agricultural use, its production has ceased in most countries before year 2000. However, due to the extensive use in the past, HCB contamination is still a serious environmental problem. Furthermore, HCB is still being released into the environment as an unintended byproduct in chemical processes, by the incomplete combustion and as an impurity in pesticides as well as from the stockpiles and disposal of HCB wastes (Bailey, 2001). It should be also noted that the atmosphere is the major transport route for HCB global distribution as well as the major exposure route for human. Its atmospheric concentrations are now fairly uniform, varying by less than an order of magnitude at background sites (Wang et al., 2010). However, the highest HCB air concentrations are still found in historical source regions, indicating that there are some ongoing primary or secondary emissions (Jaward et al., 2005). Due to its semi-volatile nature, the octanol/air partition coefficient between 10^7 and 10^8 , and relatively long atmospheric half-life (Barber et al., 2005), HCB evaporation from environmental reservoirs (the secondary emission) sustains atmospheric concentrations that are relatively high even decades after its main primary emissions have been eliminated, i.e. within an order of magnitude of those from primary emissions. Thus, the levels of HCB in air will continue to decrease at a very slow rate and, consequently, the atmospheric HCB will continue to attract considerable scientific and regulatory interest.

The major atmospheric degradation process of POPs is their oxidation by hydroxyl radicals (Atkinson, 1994; Guesten et al., 1995; Vereecken and Francisco, 2012). Analogous or similar oxidation processes (Sabljic and Peijnenburg, 2001; Stefanic et al., 2009) are also important for biodegradation of POPs in terrestrial and aquatic systems (Rucker and Kummerer, 2012; Sabljic and Nakagawa, 2014). However, only a limited data are available on the

atmospheric oxidation of HCB. There is only a single experimental study (Brubacker and Hites, 1998) where degradation rates were measured for the gas-phase reaction of hydroxyl radical with HCB in the narrow temperature range, i.e. 347–386 K, which is outside the environmentally relevant temperature range, i.e. 230–330 K. Furthermore, there is no information or theoretical study on the reaction mechanism or reaction-path dynamics of this important atmospheric degradation process. Thus, the main objective of this study is to obtain those valuable missing information on the reaction mechanism and kinetics of HCB oxidation by hydroxyl radical.

The only relevant tropospheric oxidation pathway for HCB is the addition of hydroxyl radical on aromatic ring (Atkinson, 1994), Eq. (1).

In our previous studies on monosubstituted halobenzenes (Kovacevic and Sabljic, 2013a, 2013b), i.e. chlorobenzene and fluorobenzene, it was demonstrated that the quantum chemical MP2 and G3 methods can supply valuable information on the reaction mechanism of hydroxyl radical addition to simple haloaromatic systems as well as on the corresponding thermodynamic data. Those results coupled with the RRKM (Rice–Ramsperger–Kassel–Marcus) kinetic theory have also successfully reproduced the experimental reaction rates and unusual temperature dependence for the addition of hydroxyl radicals to chlorobenzene (Kovacevic and Sabljic, 2013a) and fluorobenzene (Kovacevic and Sabljic, 2013b). In this study we will apply the same strategy to obtain valuable missing information on the reaction mechanism and reaction-path dynamics of atmospheric oxidation of model POP, i.e. hexachlorobenzene. Furthermore, this study will also supply the reliable reaction rates and temperature dependence for the addition of hydroxyl radicals on HCB in the environmentally relevant temperature range, i.e. 230–330 K.

2. Computational methods

Potential energy surface was investigated by optimizing geometries of stationary points and confirming them with frequency calculations. Geometries and frequencies were calculated using MP2/6-311G(d,p) method. The unrestricted wavefunction was used for radical species. IRC calculations, using Gonzales-Schlegel method in mass weighted coordinates, were performed to confirm the connection between transition state and minima in each reaction pathway. Geometry, frequency and IRC calculations were conducted using GAMESS program (Schmidt et al., 1992). Single point energies were calculated with G3 method (Curtiss et al., 1998, 1999) on the optimized minima and transition states using Gaussian program package (Frisch et al., 2004). The error in G3 calculations, caused by spin contamination were analyzed, by computing energy correction factors from G3 method: with and without spin projection. The error analysis is shown in the Table A.1

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