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Mechanistic and kinetic investigation on OH-initiated oxidation of tetrabromobisphenol A

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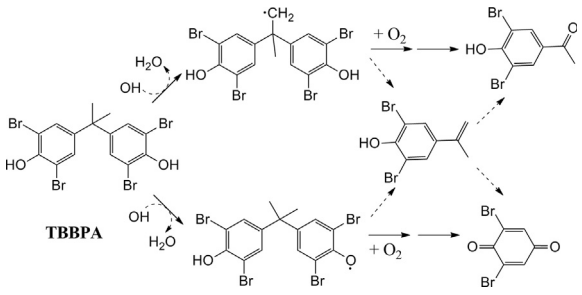
HIGHLIGHTS

- OH radical prefers to abstract alkyl and phenolic hydrogen atoms from tetrabromobisphenol A (TBBPA).
- Total rate constant increases with temperature.
- Main products include brominated phenol and benzoquinone.
- Association of two molecules of phenolic radicals produces a stable complicated compound.

GRAPHICAL ABSTRACT



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ABSTRACT

Detailed mechanism of the OH-initiated transformation of tetrabromobisphenol A (TBBPA) has been investigated by quantum chemical methods in this paper. Abstraction reactions of hydrogen atoms from the OH groups and CH_3 groups of TBBPA are the dominant pathways of the initial reactions. The produced phenolic-type radical and alkyl-type radical may transfer to 4,4′-(ethene-1,1-diyl)*bis*(2,6-dibromophenol), 4-acetyl-2,6-dibromophenol and 2,6-dibromobenzoquinone at high temperature. In water, major products are 2,6-dibromo-*p*-hydroquinone, 4-isopropylene-2,6-dibromophenol and 4-(2-hydroxyisopropyl)-2,6-dibromophenol resulting from the addition reactions. Total rate constants of the initial reaction are 1.02×10^{-12} cm^3 molecule^{-1} s^{-1} in gas phase and 1.93×10^{-12} cm^3 molecule^{-1} s^{-1} in water at 298 K.

1. Introduction

Tetrabromobisphenol A (TBBPA) is a worldwide used commercial flame retardant. It can be used either as additive or reactive flame retardant. TBBPA may migrate into the environment during the production, lifetime, recycling (hydrometallurgy) or destruction of the waste electrical and electronic equipment. TBBPA is extensively found in the environment, such as air dust, water, bird, fish, breast milk, grain, etc (Shi et al., 2009; Johnson-Restrepo et al., 2008; Inoue et al., 2003; Kefeni et al., 2011; Tollback et al., 2006). Solid waste is one of the highest emission sources of TBBPA to environment (Zhou et al., 2014). Indoor air or diet is significant exposure to TBBPA of human beings (Shi et al., 2009; Kefeni et al., 2011; Di Napoli-Davis and Owens, 2013; Schreder and La Guardia, 2014). In dust sample collected from electronic matrices, the values range from lower than the detection limit to 513 ng/g (Di Napoli-

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Davis and Owens, 2013). TBBPA affects various aspects of mammalian and human physiology (Hendriks et al., 2012; Grasselli et al., 2014). The concentration of TBBPA in surface water is quite high, and hence very toxic to the aquatic organisms (He et al., 2013).

Various experiments have been performed on the photochemical transformation of TBBPA under oxidative or reductive conditions (Li et al., 2012; Eriksson et al., 2004a; Debenest et al., 2010; Barontini et al., 2004; Huang et al., 2013; Abdallah and Harrad, 2011; Grabda et al., 2011). Tribromobisphenol A (TriBBPA), dibromobisphenol As (DiBBPAs), monobromobisphenol A (MonoBBPA), bisphenol A (BPA) and polybrominated phenols are proved to be major products of TBBPA under anoxic conditions (Liu et al., 2013; Ronen and Abeliovich, 2000; Voordeckers et al., 2002). Notably, the hazardous contaminants polybrominated dibenzo-*p*-dioxins (PBDDs)/dibenzofurans (PBDFs) are detected with trace amount under combustion experiments of TBBPA (Wichmann et al., 2002) and printed circuit boards containing TBBPA (Ortuño et al., 2014a, 2014b). Both hydroxylation and debromination are important pathway according to the identified products in the decomposition of TBBPA (Zhong et al., 2012a; Zhang et al., 2012; Xu et al., 2011). Debromination is preferred under acidic conditions (Zhu et al., 2013). In the presence of Iron, TBBPA undergo sequent debromination to Tri-, Di-, Mono-BBPAs and BPA (Luo et al., 2012). Oxidative degradation is complex and the products are diverse. 2,6-Dibromophenol (2,6-DBP), 2,6-dibromo-4-isopropenylphenol and its derivatives are found to be main products, which may be the precursors of brominated dibenzo-*p*-dioxins and dibenzofurans (Zhu et al., 2013; Marongiu et al., 2007). Eriksson et al. have proposed that the cleavage between isopropyl group and one of the benzene rings is the primary photochemical process (Eriksson et al., 2004a). Confusingly, according to the results of Altarawneh et al., a loss of methyl group instead of the rupture of the isopropylidene linkage is the preferred pathway in the gas phase (Altarawneh and Dlugogorski, 2014). Besides, various products are found in different experiments. Important intermediates are not available due to their short lives, so it is difficult to investigate the detailed mechanism of their photolysis in these media in the laboratory.

This study aims to explore the detail mechanism of the OH-initiated oxidation of TBBPA and propose the preferred pathways as well as major products using quantum chemical method. In addition, the kinetic properties are also investigated. This information will be helpful to access the major products at different temperatures.

2. Computational methods

All the thermodynamic calculations were performed using the *Gaussian* 09 program suite (Frisch et al., 2009). The geometries of all of the stable points (reactants, intermediates, and products) and transition states were optimized at the basis set of 6-31+G(d,p) using M06-2X meta hybrid functional (Zhao and Truhlar, 2008). The harmonic vibrational frequencies and zero-point vibrational energies were calculated on the same level. Intrinsic reaction coordinates (IRCs) (Gonzalez and Schlegel, 1989) were performed to verify the connections between the stable points and the transition states. To obtain more accurate energies, single-point energies of higher level were calculated at the M06-2X/6-311+G(3df,2p) level of theory, these values were corrected by the zero-point energies. Aqueous calculations were performed using the recommended SMD solvation model (Marenich et al., 2009) at the level of M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p). The rate constants of the initial reactions were calculated using canonical transition state (TST) theory including Eckart tunneling effect (Eckart, 1930). The calculations were performed using THERMO program of the recently developed MULTIWELL software (Barker et al., 2014; Barker, 2001).

3. Results and discussion

The M06-2X/6-31+G(d,p) optimized structure shows that TBBPA is centrosymmetric. The reaction heat and energy barriers of self-decomposition of TBBPA are shown in Fig. S1 in supplementary material (SM). IM and TS designate the intermediate and transition state involved in this paper, respectively. Our results are in well consistent with the experimental results (Eriksson and Eriksson, 2001) and other theoretical results (Altarawneh and Dlugogorski, 2014; Qiu et al., 2013), indicating that the level of M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p) is appropriate. Self-decomposition has been fully investigated theoretically and experimentally (Altarawneh and Dlugogorski, 2014). The cleavage of C—CH_3 bond and hydrogen migration of hydroxyl group dominate the self-decomposition of TBBPA, which is in agreement with the reference data (Altarawneh and Dlugogorski, 2014). According to Altarawneh et al., hydrogen shifts from hydroxyl group to adjacent bromo-substituted carbon atom and the C—Br bond is broken at the same time, producing phenolic radical intermediates. The process proceeds with high activation energy. However, in our calculations, only hydrogen migration is observed, and the resulted intermediates is IM8 instead of the debrominated phenolic radical intermediate. IM8 lies 21.69 kcal/mol above TBBPA, and sequently tautomerizes to ketone intermediate by releasing a Br atom. Then the ketone intermediate can abstract a hydrogen from other molecule to form TriBBPA. TriBBPA can undergo hydrogen migration, releasing bromine atom and abstracting hydrogen atom to form DiBBPAs. DiBBPAs can decompose sequently to MonoBBPA and finally BPA. This may interprete the stepwised debromination of TBBPA under reductive conditions. Interestingly, the activation energy of hydrogen migration reduces to 38.46 kcal/mol in the participation of a water molecule. The two hydrogen migrations of the transition state have been identified by the IRC results.

3.1. Reactions of TBBPA with OH radical

TBBPA can be oxidized by most oxidants (metallic oxides, hydroxyl radical, aerobic microorganism, etc). Various products have been detected under oxidative conditions, but the detailed mechanism is vague. In this paper, hydroxyl radical is selected to explore the available oxidized transformation of TBBPA.

The reaction of TBBPA with OH radical branches into seven channels: four OH-addition routes and three H-abstraction routes. As shown in Fig. 1, hydroxyl radical can attack the *ipso*-carbon atom via moderate activation energy of 1.73 kcal/mol. Then OH-adduct IM9 is produced, followed by the rapid departure of isopropyl carbon atom and C(OH) atom. The decomposition of IM9 proceeds via moderate energy barriers. 2,6-dibromo-*p*-hydroquinone (P2) and im7 are the decomposition products of IM9. P2 has been evidenced in experiments by Errikson et al. (Eriksson et al., 2004b) and Lin et al. (Lin et al., 2009) OH-addition at the *ortho*-C atom requires the lowest energy of activation, leading to the formation of IM10 which undergo three decomposition channels. Intramolecular hydrogen transfer from *ortho*-C atom to *ipso*-C atom needs to overcome a high activation energy of 47.75 kcal/mol. Then the intermediate IM12 is formed followed by the cleavage of *ipso*-propyl carbon atom with the aromatic *ipso*-carbon atom. The hydrogen migration from C(OH) group to the neighboured C(Br) atom includes a lower energy of activation (40.86 kcal/mol). The bromine atom departs at the same time, leading to hydroxylated TriBBPA (P6). In addition, hydrogen atom from CH(OH) can be abstracted by oxidants (O_2, OH radical, etc), generating hydroxylated TBBPA (P7).