

代表文章 10

多氯联苯在大气中主要存在于气相当中，且可能经历大气氧化降解过程，尤其是由 OH 自由基引发的氧化反应。在这项工作中，OH 自由基引发的最具毒性的多氯联苯同系物 3,3',4,4',5-五氯联苯（PCB126）的大气氧化机理被用量子化学的方法所研究。重要的基元反应速率常数被用 RRKM 理论估算。PCB126 与 OH 自由基的氧化反应产物包括 3,3',4,4',5-五氯联苯酚，氯苯酚，2,3,4,7,8-五氯二苯并呋喃，二醛，3,3',4,4',5-五氯-5'-硝基联苯以及 4,5-二氯-2-硝基苯酚。特别地，PCBs 的大气氧化形成多氯二苯并呋喃（PCDFs）的过程被第一次揭示。298K, 1 atm 条件下，OH 加成反应的总包速率常数是 $2.52 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 。由 OH 自由基决定的 PCB126 的大气寿命大约是 47.08 天，这表明 PCB125 可被从局域到全球范围内远距离传输。



Theoretical perspectives on the mechanism and kinetics of the OH radical-initiated gas-phase oxidation of PCB126 in the atmosphere

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HIGHLIGHTS

- A comprehensive mechanism of OH-initiated oxidation of PCB126 was investigated.
- The formation of PCDFs from the oxidation of PCBs is determined for the first time.
- The rate constants for key elementary reactions were estimated by the RRKM theory.
- The atmospheric lifetime of PCB126 determined by OH radicals is about 47.08 days.

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ABSTRACT

Polychlorinated biphenyls (PCBs) primarily exist in the gas phase in air and may undergo atmospheric oxidation degradations, particularly the oxidation reaction initiated by OH radicals. In this work, the mechanism of the OH radical-initiated atmospheric oxidation of the most toxic PCB congener 3,3',4,4',5-pentachlorobiphenyl (PCB126) was investigated by using quantum chemistry methods. The rate constants of the crucial elementary reactions were estimated by the Rice–Ramsperger–Kassel–Marcus (RRKM) theory. The oxidation products of the reaction of PCB126 with OH radicals include 3,3',4,4',5-pentachlorobiphenyl-ols, chlorophenols, 2,3,4,7,8-pentachlorodibenzofuran, 2,3,4,6,7-pentachlorodibenzofuran, dialdehydes, 3,3',4,4',5-pentachloro-5'-nitro-biphenyl, and 4,5-dichloro-2-nitrophenol. Particularly, the formation of polychlorinated dibenzofurans (PCDFs) from the atmospheric oxidation of PCBs is revealed for the first time. The overall rate constant of the OH addition reaction is $2.52 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm. The atmospheric lifetime of PCB126 determined by OH radicals is about 47.08 days which indicates that PCB126 can be transported long distances from local to global scales.

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1. Introduction

Polychlorinated biphenyls (PCBs), a group of persistent organic pollutants (POPs), have been commercially produced and used as coolants, insulating fluids and stabilizing additives since 1929 in the USA (Danse et al., 1997). It was estimated that more than 1.3 million tons of PCBs were produced in the world between 1929 and 1989. Of this amount, approximately 440 to 92,000 t has been poured into the environment (Zhang et al., 2008). The high toxicity and persistence of PCBs were confirmed in the late 1970s, and the commercial production of PCBs is now prohibited in many countries (Zhang et al., 2008; Shimazu et al., 2014). However, PCBs can still emit into the atmosphere through vaporization and incineration of PCB containing materials (Sun et al., 2006; Baek et al., 2010). Hence, PCBs can continuously contaminate the environment by long-range

atmospheric transport, and the atmospheric fate of PCBs deserves more attention.

PCB126 (3,3',4,4',5-pentachlorobiphenyl), a coplanar dioxin-like PCB, is a potent aryl hydrocarbon receptor (AhR) agonist (Johansson et al., 2006; Lopez Garcia et al., 1996). The binding of PCB126 to the AhR is presented in its Toxic Equivalency Factor (TEF) of 0.1 relative to that of TCDD of 1.0 (Sun et al., 2006; Lai et al., 2010). PCB126 is the most toxic among all 209 PCB congeners and has been frequently detected worldwide in the atmosphere (Hu et al., 2010; Xu et al., 2013). Ambient air samples collected from the northwest England revealed that the maximum concentration of PCB126 is up to 240 fg m^{-3} (Lohmann et al., 2000). Field measurement in the Yuen Long Station of Hong Kong showed that the air concentrations of PCB126 ranged from 20.8 to 351 fg m^{-3} (Choi et al., 2008). Due to its global distribution in air and highly toxic effects, it is critical to clarify the atmospheric oxidation of PCB126. However, to the best of our knowledge, previous researches mostly focused on the rate constants of the reactions of PCBs with OH radicals, and few studies on the reaction mechanism

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have been reported (Anderson and Hites, 1996; Bruckmann et al., 2013; Kwok et al., 1995).

PCBs present in the atmosphere primarily in the vapor phase. Extensive researches have demonstrated that oxidation reactions with OH radicals are the dominant loss processes for PCBs in the atmosphere (Anderson and Hites, 1996; Totten et al., 2002; Wania and Daly, 2002; Mandalakis et al., 2002). To elucidate the reaction mechanism of OH radical-initiated atmospheric oxidation of PCB126, a full analysis of the atmospheric processes is limited in the laboratory studies, largely due to the lack of efficient detection schemes for intermediate radical species. Therefore, with the aid of the density functional theory (DFT) and the Rice–Ramsperger–Kassel–Marcus (RRKM) method, we carried out a comprehensive theoretical investigation on the OH radical-initiated atmospheric oxidation degradation of PCB126 in the presence of O_2/NO_x , which is expected to be helpful for illuminating the atmospheric fate of PCB 126.

2. Computational method

The quantum chemical calculations were performed with the Gaussian 09 software package (Frisch et al., 2009) on a supercomputer. The geometries of the reactants, intermediates, transition states and products were optimized at the BB1K/6-31 + G(d,p) level, which has yielded satisfying results in previous studies (Qu et al., 2006). The vibrational frequencies were calculated to identify the structures obtained as true minima or first-order saddle points. The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that each transition state connects to the right minima along the reaction path. A more flexible basis set, 6-311 + G(3df,2p), was used to determine the single

point energies of various species. The overall energetic profile was constructed to locate the energetically favorable reaction pathways.

By means of the MESMER (Master Equation Solver for Multi Energy well Reactions) program (Glowacki et al., 2012), the rate constants of the crucial elementary reactions were deduced by using the Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Robinson and Holbrook, 1972). The RRKM rate constant is given by:

$$k(E) = \frac{W(E)}{h\rho(E)} \quad (1)$$

where $W(E)$ is the rovibrational sum of states at the transition state, $\rho(E)$ is density of states of reactants, and h is Planck's constant. Then, the canonical rate constant $k(T)$ is determined from the equation:

$$k(T) = \frac{1}{Q(T)} \int k(E)\rho(E) \exp(-\beta E) dE \quad (2)$$

where $Q(T)$ is the reactant partition function.

3. Results and discussion

For the purpose of verifying the reliability of the computational results, we optimized the geometries and calculated the vibrational frequencies of CCl_4 , benzene, phenol and naphthalene. The results agree well with the available experimental values, and the maximum relative errors are within 3.0% for geometrical parameters and 8.0% for vibrational frequencies (Kuchitsu, 1998; Herzberg, 1966; Shimanouchi, 1972; Hellwege and Hellwege, 1976; Martin et al., 1996).

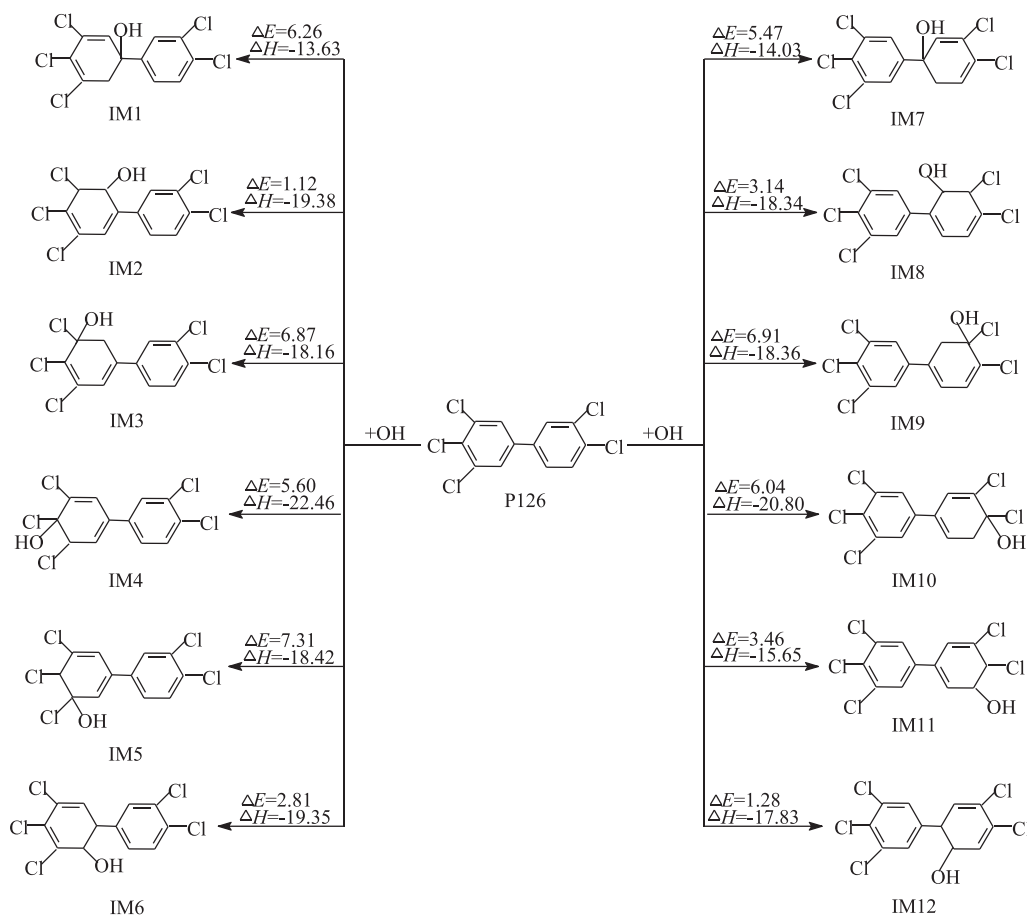


Fig. 1. The OH addition reaction scheme of PCB126 embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

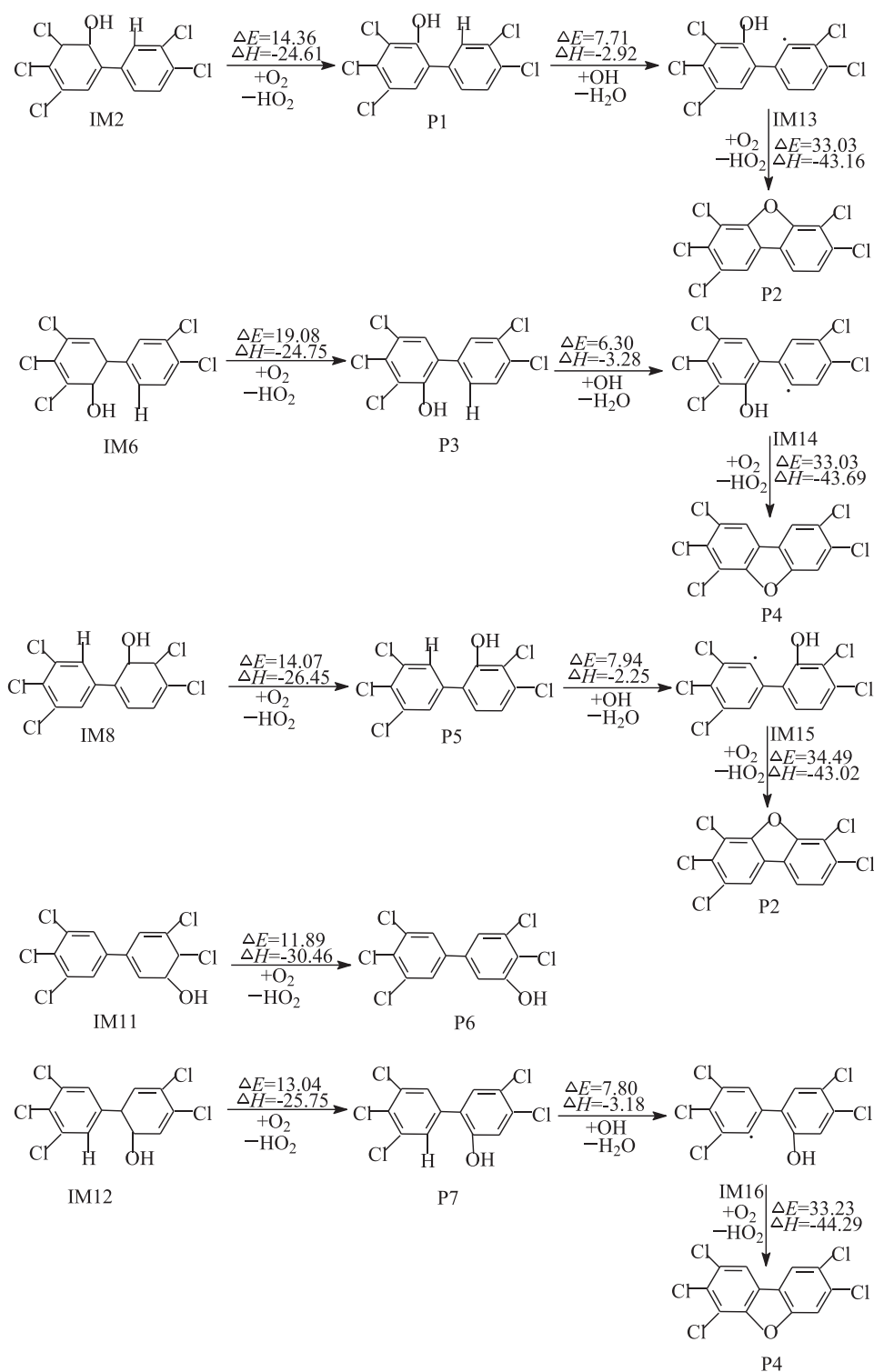


Fig. 2. The O_2 abstraction scheme of OH-PCB126 adducts (IM2, IM6, IM8, IM11 and IM12) embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

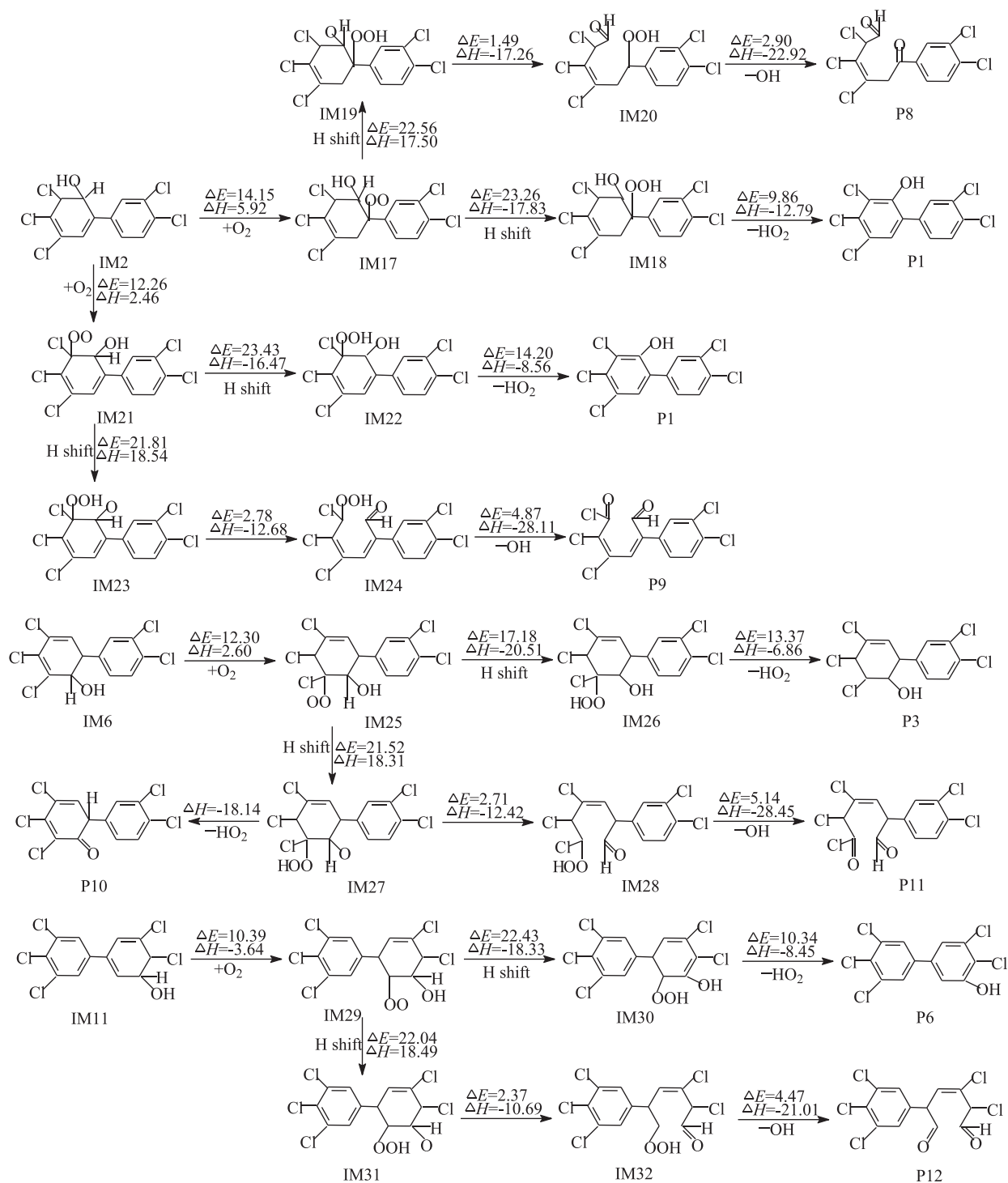
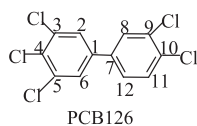


Fig. 3. The secondary reaction scheme of OH-PCB126 adducts (IM2, IM6 and IM11) embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

3.1. Reaction of with OH radicals

For convenience of description, the carbon atoms in PCB126 are numbered as follows:



There exist C=C, C-H and C-Cl bonds in the molecular structure of PCB126. Thus, addition of OH to the C=C bonds, H abstraction from the C-H bonds and Cl abstraction from the C-Cl bonds are possible pathways for the reaction of PCB126 with OH radicals. The reaction schemes embedded with the potential barriers (ΔE) and reaction heats (ΔH , 0 K) are presented in Fig. 1 and Fig. S1 of the Supporting information. It can be seen from Fig. S1 that the Cl abstraction cannot occur under the general atmospheric conditions due to the extremely high barrier and strong endothermicity. At the BB1K/6-311 + G(3df,2p) level, the potential barriers of H abstractions are

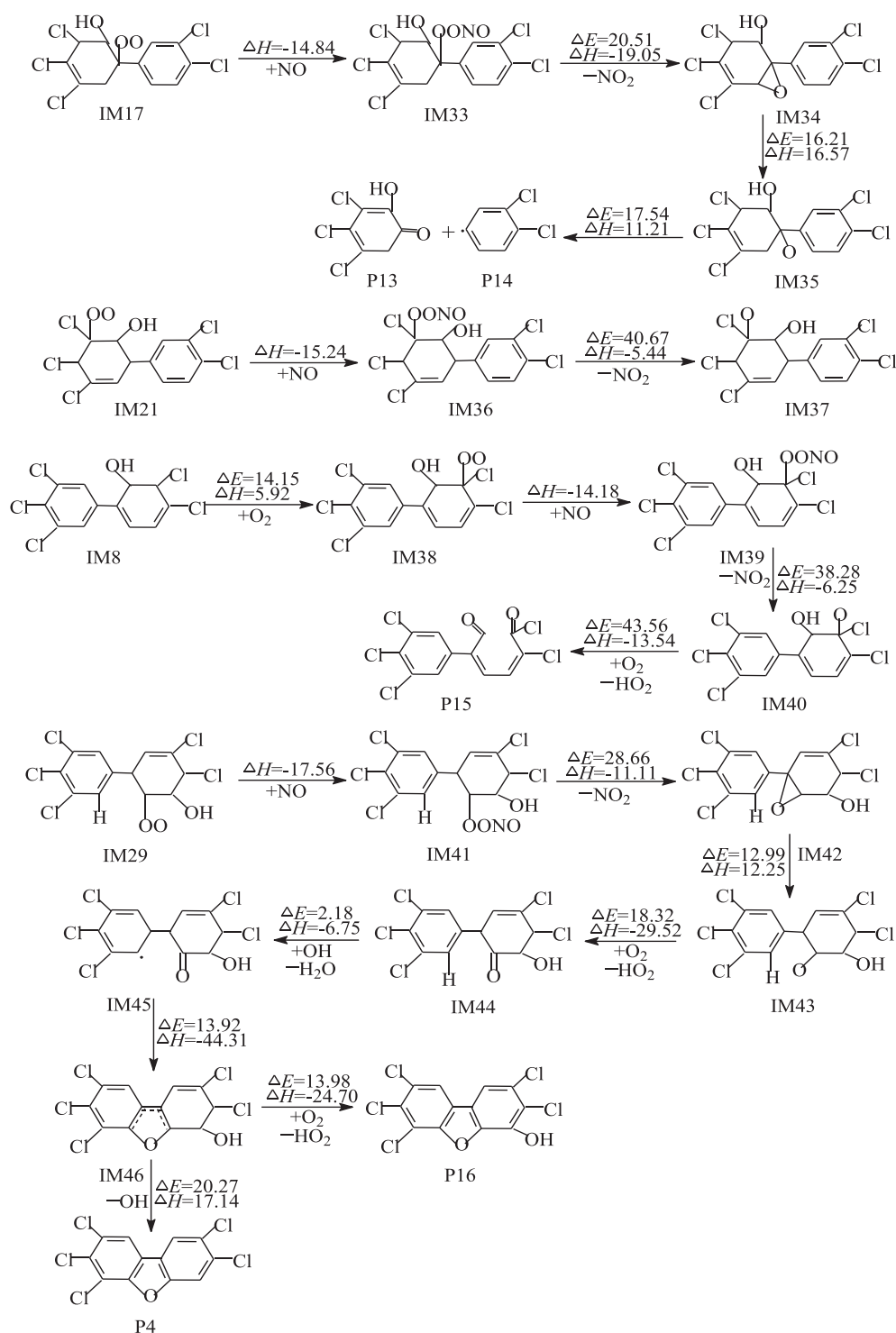


Fig. 4. The reaction scheme of IM8, IM17, IM21 and IM29 embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

6.42–6.98 kcal/mol. All H abstraction pathways are exothermic, and the reaction heats are from -3.40 to -2.34 kcal/mol. As shown in Fig. 1, the barriers of OH additions are from 1.12 to 7.31 kcal/mol, and the reaction heats are from -22.46 to -13.63 kcal/mol. The OH additions to the carbon atoms, C2, C6, C8, C11 and C12, are relatively easier because of the lower potential barriers. Clearly, the reactions of OH addition to PCB126 are the predominating processes. The resulting adducts, OH-PCB126s, from these OH addition reactions will further react with O₂/NO_x as their removal.

3.2. Secondary reactions

3.2.1. Unimolecular decomposition

The unimolecular decomposition reaction of OH-PCB126 adducts is depicted in Fig. S2. The energy-rich OH-PCB126 adducts can further react through unimolecular decomposition to yield 3,3',4,4',5-pentachlorobiphenyl-ol congeners via cleavage of the C-Cl bond and chlorophenols via cleavage of the C-C bond. The reactions of elimination of Cl are barrierless and endothermic by 0.95–5.52 kcal/mol. The

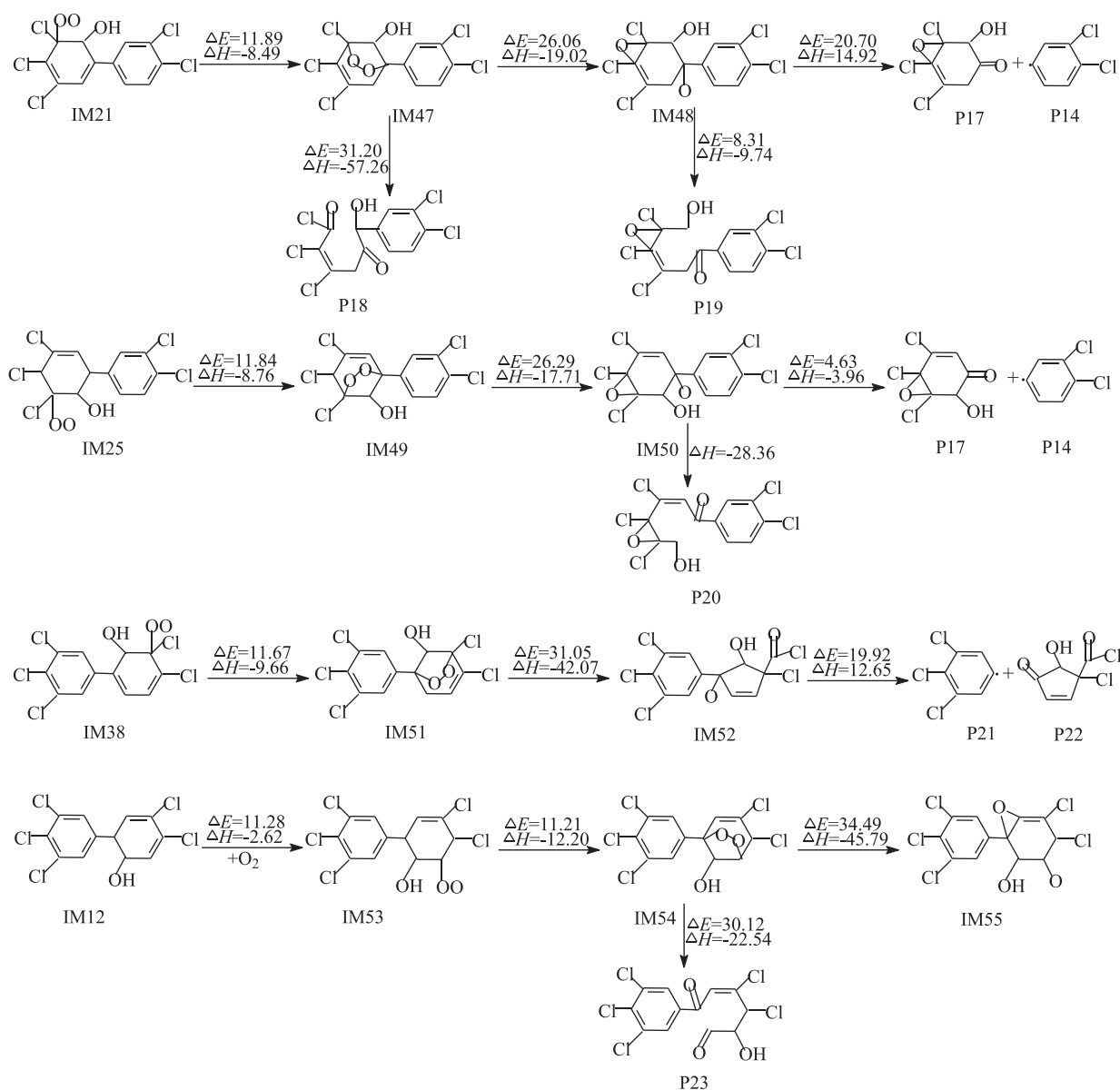


Fig. 5. The reaction scheme of IM12, IM21, IM25 and IM38 embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

potential barriers of the formation of 3,4,5-trichlorophenol and 3,4-dichlorophenol are calculated to be 19.77 and 27.46 kcal/mol, respectively. Chlorophenols have been demonstrated to be the predominant precursors of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) (Xu et al., 2010).

3.2.2. Reactions with O_2

As shown in Fig. 2, the OH-PCB126 adducts (IM2, IM6, IM8, IM11 and IM12) are unstable energy-rich radical intermediates that can readily react with molecular oxygen to form 3,3',4,4',5-pentachlorobiphenyl-ol congeners (P1, P3, P5, P6 and P7) through the H abstraction mechanism. The potential barriers of these H abstraction processes are 11.89–19.08 kcal/mol at the BB1K/6-311 + G(3df,2p) level. The processes are strongly exothermic by 24.61–30.46 kcal/mol. Comparison of the reaction pathways presented in Fig. 2 shows that the H abstraction by O_2 from the OH-PCB126 adduct IM11 has the lowest barrier and is energetically most favorable relative to the other H abstraction pathways. In particular, P1, P3, P5 and P7 can further react with OH radicals, followed by H abstraction by O_2 . It ultimately

results in the formation of 2,3,4,7,8-pentachlorodibenzofuran and 2,3,4,6,7-pentachlorodibenzofuran. Calculations show that the H abstraction by O_2 is the rate-determining step due to its high potential barrier. To our best knowledge, the formation of PCDFs from the atmospheric oxidation of PCBs was determined for the first time.

The reaction schemes of O_2 addition are displayed in Fig. 3. O_2 can attack on the C atom with an unpaired electron in the OH-PCB126 adduct IM2, resulting in the formation of IM17 and IM21. The subsequent reactions of IM17 and IM21 are similar, which include two reaction pathways. The first one involves three elementary steps: H shift from the O–H bond, C–C bond cleavage and elimination of OH, leading to the generation of a dialdehyde (P8). The second reaction pathway starts with H migration from the C–H bond, followed by the elimination of HO_2 , and ultimately results in the formation of 3,3',4,4',5-pentachlorobiphenyl-2-ol (P1). Calculations indicate that the processes of the H shift are the rate-determining process due to its high potential barrier. Similarly, other OH-PCB126 adducts (IM6 and IM11) also can react with O_2 to form dialdehydes and 3,3',4,4',5-pentachlorobiphenyl-ols. The difference is that the intermediate IM27

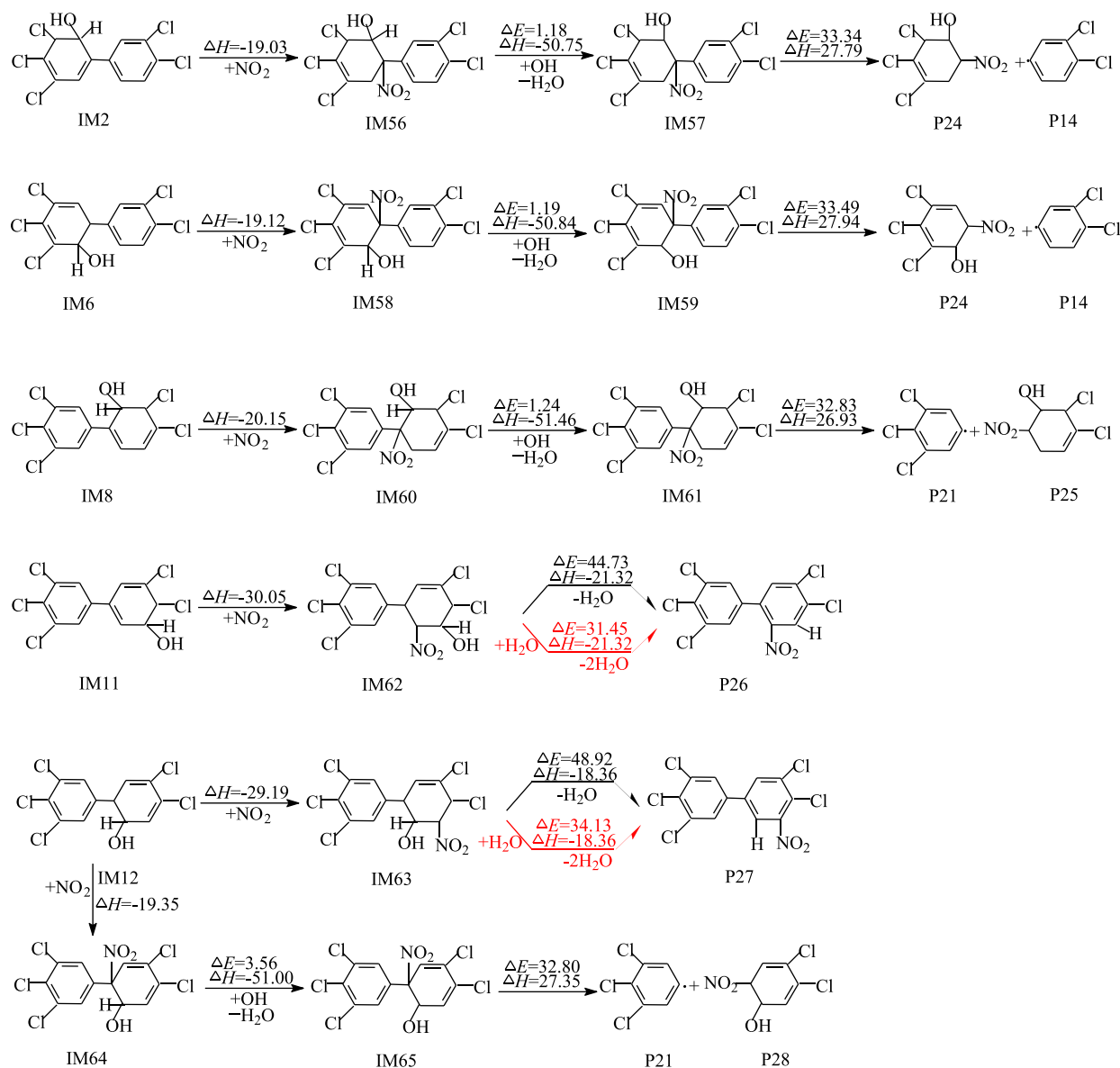


Fig. 6. The NO_2 addition scheme of OH-PCB126 adducts (IM2, IM6, IM8, IM11 and IM12) embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K.

resulted from the H shift can undergo synchronous loss of HO_2 and rearrangement to yield 3,3',4,4',5-pentachlorobiphenyl-2-one (P10). This reaction is barrierless and exothermic by 18.14 kcal/mol.

As shown in Fig. 4, the OH- O_2 -PCB126 intermediate IM17 reacts with NO, followed by the rupture of the O-ONO bond and cleavage of the C-O and C-C bond, resulting in the formation of 3,4,5-trichloro-6-hydroxycyclohexa-2,4-dienone (P13) and dichlorobenzene radical (P14). The reaction of NO addition is barrierless and exothermic. The intermediate IM38 that resulted from O_2 addition to IM8 also can react with NO via a barrierless addition followed by elimination of NO_2 and H abstraction by O_2 to produce a dialdehyde. By comparison, the process of H abstraction is the rate-determining step due to its high potential barrier. The reaction channel of IM29 contains eight elementary reactions: NO barrierless association, elimination of NO_2 , rupture of the C-O bond, H abstraction by O_2 , H abstraction by OH, cyclization, H abstraction by O_2 and elimination of OH. 2,3,4,7,8-Pentachlorodibenzofuran (P4) and 2,3,6,7,8-pentachlorodibenzofuran-4-ol (P16) are formed from these reactions. Calculations show that

these elementary reactions can occur readily under the general atmospheric conditions.

As shown in Fig. 5, the OH- O_2 -PCB126 intermediate IM21 can undergo cyclization to produce the bicyclic peroxy radical (IM47). The potential barrier of this reaction is calculated to be 11.89 kcal/mol and the process is exothermic by 8.49 kcal/mol. The ensuing reactions of IM47 include ring-opening and intramolecular decomposition processes, leading to the formation of P14, P17, P18 and P19. The reaction channel of IM25 is similar to that of IM21, with the exception of the barrierless ring-opening reaction. These processes ultimately lead to the formation of epoxides (P17 and P20) and dichlorobenzene radical (P14). The intermediate IM38 also can proceed with cyclization reaction, followed by simultaneous ring-opening and ring-closure reactions to form IM52. The elementary reaction of the cleavage of the C-C bond in IM52 results in the generation of P21 and P22. The ensuing reactions from IM54 have some similarities to those discussions above except for the formation of P23 via the intramolecular rearrangement mechanism.

3.2.3. Reactions with NO₂

The reaction scheme of the OH–PCB126 adducts and NO₂ is displayed in Fig. 6. As shown, the OH–PCB126 adducts (IM2, IM6, IM8, IM11 and IM12) can react with NO₂ to form OH–NO₂–PCB126 adducts (IM56, IM58, IM60, IM62 and IM63) via barrierless associations. These processes are strongly exothermic by 19.03–30.05 kcal/mol. The intermediates IM56, IM58 and IM60, have the similar subsequent reactions which include H abstraction by OH and intramolecular decomposition. These processes lead to the formation of 2,3,4-trichloro-6-nitrophenol, 2,3-dichloro-6-nitrophenol and chlorobenzene radicals. The calculated profiles of the potential energy surface show that the reaction of the intramolecular decomposition is the rate-determining step because of the high potential barrier. The intermediate IM62 may subsequently undergo unimolecular decomposition to yield 3',4,4',5,5'-pentachloro-2-nitro-biphenyl via the direct loss of H₂O. As shown in Fig. 6 (black arrows), the reaction barrier of the elimination of H₂O is up to 44.73 kcal/mol, so the reactions are difficult to occur under the general atmospheric conditions.

The abundant atmospheric constituent H₂O can affect the reactions via forming hydrogen bonded complexes with other molecules, such as O₃·H₂O, SO₃·H₂O, CH₃CHO·H₂O and H₂SO₄·H₂O in the atmosphere (Frost and Vaida, 1995; Meijer and Sprik, 1998; Iuga et al., 2010; Vaida and Simon, 1995). With the participation of water, the loss of water from the OH–NO₂–PCB126 adducts becomes a bimolecular reaction (OH–NO₂–PCB126 + H₂O). A six-membered ring transition state (Fig. S3 of the Supporting information) was identified, in which water molecule acts as a bridge, accepting the hydrogen from the aromatic ring and simultaneously donating another hydrogen atom to the phenolic group. The potential barrier of the loss of water via the bimolecular reaction is 13.28 kcal/mol lower than that of the direct loss of water. Similar to the mechanism presented above, the intermediate IM12 can also proceed with analogous reactions to yield 3,3',4,4',5-pentachloro-

5'-nitro-biphenyl, 4,5-dichloro-2-nitrophenol and trichlorobenzene radical.

3.3. Rate constant calculations

For the purpose of clarifying the atmospheric fate of PCB126, it is essential to determine accurate rate constants of the elementary reactions involved in the atmospheric oxidation of PCB126. Based on the BB1K/6-311 + G(3df,2p)//BB1K/6-31 + G(d,p) energies, the rate constants of the elementary reactions involved in the OH radical-initiated oxidation degradation of PCB126 were evaluated by the Rice–Ramsperger–Kassel–Marcus (RRKM) theory (Robinson and Holbrook, 1972) at 298 K and 1 atm. The RRKM method has been successfully applied to deal with several similar reactions (Glowacki et al., 2012; Zhou et al., 2011). The calculated rate constants of the important elementary reactions are listed in Table 1. The individual rate constants for the OH addition to the C₁–H–C₁₂–H bonds of PCB126 are presented as k₁–k₁₂, respectively. The overall rate constant of the OH addition reaction is denoted as k, $k = k_1 + k_2 + k_3 + k_4 + k_5 + k_6 + k_7 + k_8 + k_9 + k_{10} + k_{11} + k_{12}$. The overall rate constant k is $2.52 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm, which is consistent with the deduced rate constants of $0.3\text{--}0.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air for the reactions of pentachlorobiphenyls with the OH radical (Kwok et al., 1995). The rate constant values listed in Table 1 can be of help to the construction of specific kinetic models describing the atmospheric transformation of PCB126.

On the basis of the overall rate constant of the reaction of PCB126 with OH radicals and an average OH concentration (C_{OH}) of $9.75 \times 10^5 \text{ molecule cm}^{-3}$ (Prinn et al., 1995), from this expression:

$$\tau_{\text{OH}} = \frac{1}{k_{(\text{OH}+\text{PCB126})} \times C_{\text{OH}}}.$$

The atmospheric lifetime of PCB126 determined by OH radicals is calculated about 47.08 days, which indicates that PCB126 can be transported long distances from local to global regions.

4. Conclusions

A comprehensive theoretical research on the reaction mechanism of the OH radical-initiated atmospheric oxidation of PCB126 was investigated by using quantum chemistry methods. The rate constants of crucial reactions were determined by using the RRKM method. Three conclusions can be drawn from this study:

- (1) Compared to the H abstractions and Cl abstractions by OH radicals, the reactions of OH addition to PCB126 are the dominant processes. The OH addition to the carbon atoms C2, C6, C8, C11 and C12 is easier due to the lower potential barriers.
- (2) The OH-initiated atmospheric oxidation of PCB126 generates a class of ring-retaining and ring-opening products containing 3,3',4,4',5-pentachlorobiphenyl-ol congeners, chlorophenols, 2,3,4,7,8-pentachlorodibenzofuran, 2,3,4,6,7-pentachlorodibenzofuran, dialdehydes, 3, 3',4,4',5-pentachlorobiphenyl-2-one, dichlorobenzene radicals, 3,4,5-trichloro-6-hydroxycyclohexa-2,4-dienone, 2,3,6,7,8-pentachlorodibenzofuran-4-ol, epoxides, 2,3,4-trichloro-6-nitrophenol, 2,3-dichloro-6-nitrophenol, 3',4,4',5,5'-pentachloro-2-nitro-biphenyl, 3,3',4,4',5-pentachloro-5'-nitro-biphenyl, 4,5-dichloro-2-nitrophenol etc. The formation of polychlorinated dibenzofurans (PCDFs) from the atmospheric oxidation of PCBs was revealed for the first time.
- (3) The overall rate constant of the OH addition to PCB126 is calculated to be $2.52 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm. The atmospheric lifetime of PCB126 determined by the OH radical is about 47.08 days.

Table 1
Calculated rate constants (cm³ molecule^{−1} s^{−1}) for the crucial elementary reactions involved in the OH radical-initiated oxidation of PCB126 at 298 K and 1 atm.

Reactions	Rate constants
PCB126 + OH → OH–PCB126	(k) 2.52×10^{-13}
PCB126 + OH → IM1	(k ₁) 8.43×10^{-18}
PCB126 + OH → IM2	(k ₂) 1.15×10^{-13}
PCB126 + OH → IM3	(k ₃) 4.18×10^{-18}
PCB126 + OH → IM4	(k ₄) 2.48×10^{-17}
PCB126 + OH → IM5	(k ₅) 2.22×10^{-18}
PCB126 + OH → IM6	(k ₆) 1.31×10^{-14}
PCB126 + OH → IM7	(k ₇) 1.03×10^{-16}
PCB126 + OH → IM8	(k ₈) 6.49×10^{-15}
PCB126 + OH → IM9	(k ₉) 4.25×10^{-18}
PCB126 + OH → IM10	(k ₁₀) 1.36×10^{-17}
PCB126 + OH → IM11	(k ₁₁) 3.55×10^{-15}
PCB126 + OH → IM12	(k ₁₂) 1.14×10^{-13}
IM2 → IM17	2.65×10^{-24}
IM17 → IM18	1.46×10^{-11}
IM18 → P1	1.13×10^5
IM17 → IM19	8.97×10^{-9}
IM19 → IM20	1.00×10^8
IM20 → P8	8.17×10^8
IM2 → IM21	4.99×10^{-23}
IM21 → IM22	3.12×10^{-13}
IM22 → P1	29.3
IM21 → IM23	4.36×10^{-8}
IM23 → IM24	8.55×10^7
IM24 → P9	5.17×10^7
IM17 → IM33	4.82×10^{-13}
IM33 → IM34	4.91×10^{-3}
IM34 → IM35	5.61×10^{-5}
IM35 → P13	1.08×10^{-3}
IM45 → IM46	6.34
IM21 → IM47	9.78×10^2
IM47 → IM48	2.42×10^{-4}
IM48 → P17	1.41×10^{-5}

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Appendix A. Supplementary data

The H abstraction reaction scheme of PCB126 embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). ΔH is calculated at 0 K. The reaction scheme of the unimolecular decomposition of OH–PCB126 adducts (IM1, IM3, IM4, IM5, IM7, IM9 and IM10) embedded with the potential barrier ΔE (in kcal/mol) and reaction heat ΔH (in kcal/mol). Configuration of the transition states for the elimination of water from the OH–NO₂–PCB126 adduct (IM62). TS1: OH–NO₂–PCB126 → nitro-PCB126 + H₂O, TS2: OH–NO₂–PCB126 + H₂O → nitro-PCB126 + 2H₂O. The material is available free of charge via the Internet at <http://www.elsevier.com/>. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2015.02.061>.

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