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**Theoretical study on the reactions of a series of
polybromobenzenes with OH radicals : mechanism, kinetics
and QSAR**

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1 Abstract

Polybromobenzenes are a kind of monocyclic aromatic flame retardants which are used as a substitute for polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCE). In this paper, the reaction mechanism and rate constants for the reaction of OH radicals with a series of polybromobenzenes such as hexabromobenzene (HBB), 1,2,4,5-tetrabromobenzenes (1,2,4,5-TeBB), pentabromobenzene (PEBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT) and 2,4,5-tribromotoluene (2,4,5-TrBT) have been investigated by quantum chemical method. The reaction mechanism was obtained at the MPWB1K/6-311+g(3df,2p)//MPWB1K/6-31+g(d,p) level of theory and the rate constants were deduced over the temperature range of 200–370 K using canonical variational transition state (CVT) theory with the small curvature tunneling (SCT) method. The rate constants of OH radicals with HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT are determined to be 5.72×10^{-13} , 1.23×10^{-12} , 8.78×10^{-13} , 9.23×10^{-13} , 6.46×10^{-13} and 1.69×10^{-12} at 298 K and 1 atm, respectively. The estimated atmospheric lifetimes of HBB (20.08 days), 1,2,4,5-TeBB (9.65 days), PEBB (13.5 days), PBEB (12.9 days), PBT (18.4 days) and 2,4,5-TrBT (7.0 days) determined by OH radicals indicate that polybromobenzenes have the potential for long-range transport. The genetic function approximation (GFA) is used to study the quantitative structure–activity relationship. The coefficients indicate that the E_{LUMO} has the highest correlation to $\log k_{\text{OH}}$.

Keywords: Polybromobenzenes; OH radicals; Reaction Mechanism; Rate Constants;

Atmospheric Lifetime

2 Introduction

Brominated flame retardants (BRFs) have been widely used in many commercial products such as electrical products, textiles and furnishings to prevent or retard the initial phase of a developing fire [1]. Two of the mostly produced and used BRFs in the 1990s and 2000s, Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD), are known to be harmful for the environment and humans because of their toxicity, bioaccumulation, persistence and long-range transport potential in the environment [2-4]. As a result, tetra-, penta-, hexa- and hepta-BDEs and HBCD have been banned under the Stockholm Convention on Persistent Organic Pollutants (POPs) [5]. Restrictions of PBDEs and HBCD have led to the increasing production and

use of some substituted flame retardants such as polybromobenzenes.

Polybromobenzenes are a kind of monocyclic aromatic compounds substituted by several bromine atoms and/or small alkyl groups, such as hexabromobenzene (HBB), pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), pentabromobenzene (PEBB), 2,4,5-tribromotoluene (2,4,5-TrBT) and 1,2,4,5-tetrabromobenzenes (1,2,4,5-TeBB), etc. These compounds have been used as alternative BFRs in polyester, latex, textiles, electronics and plastic goods [6-7]. With relatively high vapor pressure, they may enter into the atmosphere during the production and consumption as well as electronic waste recycling and thermal processes such as steel production and incineration of solid waste [8-10]. China is one of the major BFRs manufactures in the world and the

occurrence of bromobenzenes has been frequently detected in atmosphere of China [8-10]. Among 89 atmospheric samples in North China, PBEB was detected in 88 samples; 2,4,5-TrBT was detected in 85 samples; HBB, PEBB, PBT and 1,2,4,5-TeBB were detected in all the samples. At the same time, the concentrations of PBT, PEBB, HBB, PBEB, 2,4,5-TrBT, 1,2,4,5-TeBB were up to 15700, 5550, 4870, 4700, 2360 and 1950 pg/sample, respectively [10]. To make things worse, some polybromobenzenes have been shown to bioaccumulate in wildlife and to be hepato-toxic to mice [11-13]. The high concentration, detection frequency and adverse effects on both wildlife and animals make it important to investigate the lifetimes of polybromobenzenes in the atmosphere.

Analysis of gas-particle fractions in the atmosphere shows that

bromobenzenes tend to exist mainly in the gas phase, especially in the high temperatures of summer [14]. Similar to other brominated flame retardants, gas-phase bromobenzenes are expected to undergo photolysis and reactions with atmospheric oxidants, such as hydroxyl (OH), nitrate (NO₃) radicals and O₃. The reaction with OH radicals is considered to be an important removal process of gas-phase bromobenzenes. More attention has been paid to investigate their atmospheric concentration and toxicity, and few studies have been focused on the removal processes of gas-phase bromobenzenes, partly because transformation processes under real conditions are hard to simulate experimentally since the results depend upon many factors such as temperature, humidity, all kinds of oxidants and so on. Quantum chemical method can provide accurate predictions for the reaction

mechanism and offer kinetic data for key elementary reactions. This method has been successfully used to investigate the reactions of OH radicals with some other brominated flame retardants such as 2,4,4'-tribrominated diphenyl ether (BDE-28), 2,2',4,4'-tetrabrominated diphenyl ether (BDE-47) and 2,4-dibrominated diphenylether (BDE-7) [15-17].

In this paper, the reaction mechanism and kinetics for the reaction of OH radicals with six polybromobenzenes are investigated by quantum chemical method. These six polybromobenzenes are hexabromobenzene (HBB), 1,2,4,5-tetrabromobenzenes (1,2,4,5-TeBB), pentabromobenzene (PEBB), pentabromoethylbenzene (PBEB), pentabromotoluene (PBT) and 2,4,5-tribromotoluene (2,4,5-TrBT).

3 Computational Methods

3.1 Geometry optimization

All the geometries, frequencies and energies of reactants, intermediates, transition states and products were performed using Gaussian 03 package [18]. The geometrical parameters were optimized at the MPWB1K level with a standard basis set 6-31+G(d,p) [19-21]. The vibrational frequencies were also calculated at the same level in order to determine the nature of the stationary points and the zero-point energy (ZPE) [22]. MPWB1K is a hybrid density functional theory model based on the modified Perdew and Wang 1991 exchange functional and Becke's 1995 meta correlation functional and gives excellent performance for thermochemistry, thermochemical kinetics, hydrogen bonding and weak interactions [23-24]. An intrinsic reaction coordinate (IRC) analysis was performed

to make sure every transition state connect the designated reactants and products [25]. For a more accurate evaluation of the energetic parameters, a more flexible basis set, 6-311+G(3df,2p), was performed to determine the energies of various species [26].

3.2 Kinetic calculation

The kinetics calculation was carried out using Polyrates 9.7 program [27]. Rate constants of each elementary step involved in this study were estimated using canonical variational transition-state (CVT) theory [28-30]. Quantum tunneling effects were performed with small curvature tunneling (SCT) method [31].

3.3 Quantitative structure–activity relationship.

The genetic function approximation (GFA) [32] in the Materials studio package is used to analyze the relationship between the OH radical

addition rate constants and configuration parameters [33]. In order to improve the correlation of mathematic model, the exceptional values in test data are eliminated after outlier analysis.

4 Results and discussion

In order to confirm the reliability of the theoretical calculations, we optimized the geometries and calculated the vibrational frequencies of a similar structure, benzene. The maximum relative errors are less than 1% for geometrical parameters and less than 3% for vibrational frequencies [34-35]. Moreover, MPWB1K/6-31+g(d,p) method has been successfully used to investigate the reaction mechanism of OH radicals with some brominated flame retardants [15-17].

4.1 Reaction mechanism

Benzene

The reaction mechanisms of OH radicals with HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT are investigated at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level. The optimized structures of six polybromobenzenes are listed in Fig. 1. The reaction pathways including reaction enthalpy (ΔH) and energy barrier (ΔE) of every elementary reaction are listed in Fig.2-Fig.6. The zero-point energy (ZPE) is also considered in the calculation process of reaction enthalpy (ΔH) and energy barrier (ΔE). In order to describe the reaction mechanism easily, the carbon atoms are numbered. The detailed reaction processes are discussed in the following:

4.1.1 HBB, 1,2,4,5-TeBB and

The reaction mechanism of OH radicals with HBB and 1,2,4,5-TeBB is listed in Fig.2. The carbon atoms in HBB are located in the same environment, so there is only one OH reaction pathway, pathway 1. The formation of P1 and Br is highly exothermic by 35.79 kcal/mol with a potential barrier of 3.05 kcal/mol. The optimized structure of TS1 is listed in Fig. 7. In TS1, the bond length of C atom in benzene ring and O atom in OH is 1.940 Å and bond length of C atom connected with O atom in benzene and Br atom is 1.867 Å. The formation of C-O bond and cleavage of C-Br bond occurred at the same time. The reaction process of OH and HBB is actually Br-substitution reaction process.

For 1,2,4,5-TeBB, there are two kinds of carbon atoms: carbon atom

connected with H atom (C_1 atom) and carbon atom connected with Br atom (C_2 atom). Moreover, OH radicals can abstract H atom connected with C_1 atom. Therefore, there are three reaction pathways: pathways 2-4. Pathway 2 is H atom abstraction process and the formation of IM1 and H_2O is slightly exothermic with a energy barrier of 7.64 kcal/mol. Pathways 3-4 are reaction pathways for OH addition to two different carbon atoms. Among these three reaction pathways, pathway 3 is more energetically feasible than the other two pathways. TS2 is the corresponding transition state for H abstraction process. The bond lengths of C_1 -O bond and O-H bond in TS2 are 1.273 and 1.178 Å, respectively. TS3 and TS4 are the transition states for OH addition to C_1 atom and C_2 atom, respectively. Similar to pathway 1, the formation of C-O bond and cleavage of

C-Br bond occurred at the same time in pathway 4.

The reaction mechanism of OH radicals with Benzene is also listed in Fig. 2 to investigated the influence of Br atoms on the phenyl ring. Pathway 5 and pathway 6 are the corresponding reaction pathways for H atom abstraction and OH addition, respectively. TS5 and TS6 are the corresponding transition states for H abstraction process and OH addition process, respectively.

Comparison between pathway 2 and pathway 5 indicates that the existence of Br atom makes the C_1 -H bond in abstraction transition state longer and H-O bond shorter. Moreover, existence of Br atom makes the occurrence of H abstraction process more difficult. Due to the existence of symmetry in 1,2,4,5-TeBB, the existence of Br atom makes the addition process of

OH to C₁ atom more easily.

4.1.2 PEBB, PBEB and PBT

The reaction mechanism of OH radicals with PEBB is listed in Fig.3. Pathway 7 is H atom abstraction process. As there are four different carbon atoms (C₁-C₄) in PEBB, four OH addition pathways are found (pathways 8-11). Pathway 7 is H abstraction process with a potential barrier of 8.39 kcal/mol. The optimized transition states for pathways 7-11 are listed in Fig. 8. TS7 is the corresponding transition state for H abstraction process, in which C₁-H bond is 1.274 Å and H-O bond is 1.174 Å. C₁-H bond in TS7 with five Br atoms is longer than that in TS2 with four Br atoms and H-O bond in TS7 with five Br atoms is shorter than that in TS2 with four Br atoms. Moreover, the energy barrier of pathway 7 is higher than that

of pathway 2, which confirms the conclusion that the increase of Br atom number makes the H abstraction process more difficult. TS8, TS9, TS10 and TS11 are the corresponding transition states for OH addition to C₁, C₂, C₃ and C₄, respectively. Pathway 8 is the addition of OH radicals to C₁ atom connected with H atoms and pathways 9-11 are addition of OH radicals to C₂, C₃ and C₄ atoms, all of which are connected with Br atoms. Among four addition pathways, pathway 8 is more energetically feasible than other three addition pathways, meaning that the addition of OH radicals to C atoms connected with H atoms is more easily than OH addition to other C atoms connected with Br atoms. The shorter C-O bond in TS8 than those in TS9-TS11 also confirms the conclusion.

The reaction pathways for the reaction of OH radicals with PBEB are

listed in Fig. 4. As there are two different H atoms in the $-C_2H_5$ group of PBEB, two abstraction processes are found (pathways 12-13). The abstraction and addition transition states are listed in Fig. 8. . Similar to PEBB, there are four addition processes for PBEB (pathways 14-17). Six pathways are all listed in Fig. 4. Pathway 12 is OH abstraction from H atoms in the $-CH_3$ group. Pathway 13 is OH abstraction from H atoms in the $-CH_2-$ group. Pathway 12 is more energetically feasible than pathway 13, indicating that the H atoms in the $-CH_2-$ group are more activated than the H atoms in the $-CH_3$ group. Similar to PEBB, OH addition to C atom connected with $-C_2H_5$ group (pathway 14) is more energetically feasible than other addition pathways.

The reaction pathway for OH radicals with PBT is similar to the reaction pathways of OH radicals with

PEBB and PBEB. H abstraction process (pathway 18) and OH addition to C atom adjacent to $-CH_3$ group (pathway 19) are energetically feasible pathways. The structures of PEBB, PBT and PBEB are very similar. Five H atoms in benzene ring of PEBB, PBT and PBEB are substituted by Br atoms. In PBT, the last H atom in benzene ring is substituted by $-CH_3$ group and the last H atom in benzene ring of PBEB is substituted by $-C_2H_5$ group. It is interesting to compare the abstraction process and addition processes occurred in the similar position of PEBB, PBT and PBEB. Comparison of all abstraction processes involved in PEBB, PBT and PBEB (pathway 7, pathway 12, pathway 13 and pathway 18) indicates that OH abstraction from $-CH_3$ group of PBT is more energetically feasible than OH abstraction from $-C_2H_5$ group of PBEB and $-H$ group of PEBB. For both PEBB,

PBT and PEBB, OH addition to C₁ atom is more energetically feasible than OH addition to other C atoms. This is because -H, -CH₃ and -C₂H₅ are all electron-donating groups, whereas -Br is electron-withdrawing group. Pathway 8, pathway 14 and pathway 19 are addition processes for OH addition to C₁ atoms connected with -H, -C₂H₅ and -CH₃. Pathway 19 is more energetically feasible than pathway 8 and pathway 14. Similar result is also observed for OH addition to C₂ atoms connected with -H, -C₂H₅ and -CH₃. Pathway 20 is more energetically feasible than pathway 9 and pathway 15. This can be explained by the combination effects of electron-donating group effect and steric hindrance effect of -CH₃ and -C₂H₅. Totally different results are found for OH addition to C₃ and C₄ atoms connected with -H, -C₂H₅ and -CH₃. For OH addition to C₃ and C₄ atoms, OH

addition to C atoms connected with -H is the most energetically feasible process and OH addition to C atoms connected with -CH₃ is more energetically feasible than OH addition to C atoms connected with -C₂H₅.

The only difference between PEBB, PBT and PBEb is that there are different substitution groups connected with C₁ atom of phenyl group. The comparison between similar addition processes shows that for OH addition to C₁ and C₂ atoms, OH addition to C atoms in PBT is the most energetically feasible pathway, OH addition to C atoms in PEBB is the least energetically feasible pathway. For OH addition to C₃ and C₄ atoms, -OH addition to C atom in PEBB is the most energetically feasible pathway and OH addition to C atom in PBEb is the least energetically feasible pathway.

4.1.3 2,4,5-TrBT

No symmetry is found in 2,4,5-TrBT, so there are nine reactions pathways for the reaction of OH radicals with 2,4,5-TrBT, as are shown in Fig. 6. Pathways 23-25 are H atom abstraction processes and pathways 26-31 are OH addition processes. Among three abstraction pathways, pathway 23 is more energetically feasible than other two abstraction pathways. Among six addition pathways, OH addition to C atom adjacent to -CH₃ group (C₁) and C atoms adjacent to H atoms (C₂ and C₅) are more energetically feasible than other four addition processes. All the transition states for the reaction of OH radicals with 2,4,5-TrBT are listed in Fig. 9.

4.2 Rate Constant Calculations

Canonical variational transition

state theory (CVT) with small-curvature tunneling (SCT) contribution has been successfully performed to estimate the rate constants of OH radicals with some brominated flame retardants [16-17]. Moreover, our calculated rate constant for OH radicals with benzene at 298K and 1 atm ($2.06 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) agrees well with the experimental value ($1.59 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [36]. In this paper, this method has also been used to calculate the rate constants for the reaction of OH with HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT, based on the geometries and energies at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level. A suitable temperature range of 200–370 K was chosen to study the relationship between the temperature and rate constant at 1 atm. The CVT/SCT values are expressed in the Arrhenius form, as are shown in

Table 1. The pre-exponential factors, the activation energies and the rate constants can be obtained from the Arrhenius form.

By the calculation, the rate constants of OH radicals with HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT are determined to be 5.72×10^{-13} , 1.23×10^{-12} , 8.78×10^{-13} , 9.23×10^{-13} , 6.46×10^{-13} and 1.69×10^{-12} at 298 K and 1 atm, respectively. According to the overall rate constants and a typical OH concentration (C_{OH}) of 9.75×10^5 molecule cm^{-3} , atmospheric lifetime of HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT determined by OH radical can be obtained by the expression [37]:

$$\tau_{OH} = \frac{1}{k_{tot} \times C_{OH}}$$

where τ_{OH} is atmospheric lifetime of HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT determined by OH radicals; k_{tot} is the overall rate constant

for the reaction of HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT with OH radicals; C_{OH} is a typical OH concentration. The atmospheric lifetimes of HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT are estimated to be 20.08 days, 9.65 days, 13.5 days, 12.9 days, 18.4 days and 7.0 days, respectively.

4.3 Relation between rate constants and the configuration parameters

The configuration parameters include molecular volume (M.V), molecular weight (M.W), the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), and the dipole moment (D. M), the highest positive charge (Q^+), the lowest negative charge (Q^-), the total energy of the molecular (E). After the frequency at the MPWB1K/6-31+G(d,p) level are

calculated, the configuration parameters can be obtained and listed in Table 2.

After performing genetic function approximation (GFA) calculations, we obtained the expressions connecting $\log k_{\text{OH}}$ to the configuration parameters. The equation shows how the configuration parameters influence rate constants.

$$\log k_{\text{OH}} = 0.00149 \times \text{M.V} + 19.553 \times E_{\text{LUMO}} + 0.110 \times \text{D.M} + 0.499 \times Q^- - 11.493, \\ R^2 = 0.9999, R^2_{\text{cv}} = 0.9587.$$

As shown by the R^2 and R^2_{cv} in model, the $\log k_{\text{OH}}$ is well correlated to the variables. The relativity between the actual values and predicted values is excellent as shown in the Fig. 10. The $\log k_{\text{OH}}$ increases as M.V, E_{LUMO} , D.M, and Q^- increase. The coefficients indicate that the E_{LUMO} has the highest correlation to $\log k_{\text{OH}}$.

5 Conclusions

In this paper, the reaction mechanisms and kinetics for the reaction of OH radicals with HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT were investigated. Some valuable conclusions can be drawn:

1. The OH addition process is more energetically feasible than Br-substitution process. The energy barriers of abstraction pathways increased with the increasing bromine atom number, showing that bromine atom decrease the activity of the phenyl ring.
2. The rate constants and atmospheric lifetimes of HBB, 1,2,4,5-TeBB, PEBB, PBEB, PBT and 2,4,5-TrBT show that polybromobenzenes have the potential for long-range transport.
3. The rate constants increase as M.V, E_{LUMO} , D.M, and Q^- increase. The coefficients indicate that the E_{LUMO} has the highest correlation to $\log k_{\text{OH}}$.

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Figure captions

Fig. 1 Optimized structures of six polybromobenzenes. Unit: Å. Distances are in angstroms. Gray sphere, C; White sphere, H; Red sphere, O; Green sphere, Br.

Fig. 2 Reaction of OH radicals with HBB, 1,2,4,5-TeBB and Benzene. Unit: kcal/mol. ΔE , the reaction potential barrier; ΔH , the reaction enthalpy (0 K).

Fig. 3 Reaction of OH radicals with PeBB. Unit: kcal/mol. ΔE , the reaction potential barrier; ΔH , the reaction enthalpy (0 K).

Fig. 4 Reaction of OH radicals with PBEB. Unit: kcal/mol. ΔE , the reaction potential barrier; ΔH , the reaction enthalpy (0 K).

Fig. 5 Reaction of OH radicals with PBT. Unit: kcal/mol. ΔE , the reaction potential barrier; ΔH , the reaction enthalpy (0 K).

Fig. 6 Reaction of OH radicals with 2,4,5-TrBT. Unit: kcal/mol. ΔE , the reaction potential barrier; ΔH , the reaction enthalpy (0 K).

Fig. 7 Optimized structures of TS1-TS6. Unit: Å. Gray sphere, C; White sphere, H; Red sphere, O; Green sphere, Br.

Fig. 8 Optimized structures of TS7-TS22. . Unit: Å. Gray sphere, C; White sphere, H; Red sphere, O; Green sphere, Br.

Fig. 9 Optimized structures of TS23-TS31. Unit: Å. Gray sphere, C; White sphere, H; Red sphere, O; Green sphere, Br.

Fig. 10 The actual values and predicted values of the total rate constant k_{OH} .

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Table 1. The rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or s^{-1}) of the crucial elementary reactions involved in the OH-initiated atmospheric reaction for HBB, 1,2,4,5-TEBB, Benzene, PEBB, PBEB, PBT and 2,4,5-TrBT over the temperature range of 200–370 K

Reactions	Arrhenius Formulas
HBB + OH $\rightarrow$ P1 + Br via TS1	$k(T) = (3.79 \times 10^{-11})\exp(2048.65/T)$
1,2,4,5-TeBB + OH $\rightarrow$ IM1 + H ₂ O via TS2	$k(T) = (1.53 \times 10^{-14})\exp(4177.64/T)$
1,2,4,5-TeBB + OH $\rightarrow$ IM2 via TS3	$k(T) = (1.15 \times 10^{-13})\exp(439.50/T)$
1,2,4,5-TeBB + OH $\rightarrow$ P2 + Br via TS4	$k(T) = (2.92 \times 10^{-13})\exp(2808.88/T)$
Benzene + OH $\rightarrow$ IM3 + H ₂ O via TS5	$k(T) = (8.23 \times 10^{-13})\exp(2963.11/T)$
Benzene + OH $\rightarrow$ IM4 via TS6	$k(T) = (1.10 \times 10^{-11})\exp(1090.24/T)$
PEBB + OH $\rightarrow$ IM5 + H ₂ O via TS7	$k(T) = (3.26 \times 10^{-13})\exp(4790.24/T)$
PEBB + OH $\rightarrow$ IM6 via TS8	$k(T) = (3.85 \times 10^{-13})\exp(694.61/T)$
PEBB + OH $\rightarrow$ P3 + Br via TS9	$k(T) = (2.12 \times 10^{-14})\exp(2605.32/T)$
PEBB + OH $\rightarrow$ P4 + Br via TS10	$k(T) = (1.17 \times 10^{-13})\exp(1510.87/T)$
PEBB + OH $\rightarrow$ P5 + Br via TS11	$k(T) = (9.36 \times 10^{-14})\exp(1103.78/T)$
PBEB + OH $\rightarrow$ IM7 + H ₂ O via TS12	$k(T) = (9.76 \times 10^{-14})\exp(756.35/T)$
PBEB + OH $\rightarrow$ IM8 + H ₂ O via TS13	$k(T) = (2.16 \times 10^{-13})\exp(570.83/T)$
PBEB + OH $\rightarrow$ IM9 via TS14	$k(T) = (4.15 \times 10^{-12})\exp(1172.60/T)$
PBEB + OH $\rightarrow$ P6 + Br via TS15	$k(T) = (6.67 \times 10^{-13})\exp(2635.94/T)$
PBEB + OH $\rightarrow$ P7 + Br via TS16	$k(T) = (3.76 \times 10^{-13})\exp(2915.66/T)$
PBEB + OH $\rightarrow$ P8 + Br via TS17	$k(T) = (3.85 \times 10^{-13})\exp(3049.25/T)$
PBT + OH $\rightarrow$ IM10 + H ₂ O via TS18	$k(T) = (4.90 \times 10^{-13})\exp(914.34/T)$
PBT + OH $\rightarrow$ IM11 via TS19	$k(T) = (2.80 \times 10^{-13})\exp(2178.59/T)$
PBT + OH $\rightarrow$ P9 + Br via TS20	$k(T) = (4.37 \times 10^{-13})\exp(961.82/T)$
PBT + OH $\rightarrow$ P10 + Br via TS21	$k(T) = (8.87 \times 10^{-14})\exp(1299.96/T)$
PBT + OH $\rightarrow$ P11 + Br via TS22	$k(T) = (1.46 \times 10^{-14})\exp(2653.39/T)$
2,4,5-TrBT + OH $\rightarrow$ IM12 + H ₂ O via TS23	$k(T) = (1.06 \times 10^{-13})\exp(2156.62/T)$
2,4,5-TrBT + OH $\rightarrow$ IM13 + H ₂ O via TS24	$k(T) = (7.07 \times 10^{-15})\exp(1188.54/T)$
2,4,5-TrBT + OH $\rightarrow$ IM14 + H ₂ O via TS25	$k(T) = (5.31 \times 10^{-14})\exp(4129.93/T)$

2,4,5-TrBT + OH → IM15 via TS26	$k(T) = (2.04 \times 10^{-13})\exp(1053.26/T)$
2,4,5-TrBT + OH → IM16 via TS27	$k(T) = (8.79 \times 10^{-14})\exp(503.87/T)$
2,4,5-TrBT + OH → P12 + Br via TS28	$k(T) = (3.82 \times 10^{-13})\exp(2620.15/T)$
2,4,5-TrBT + OH → P13 + Br via TS29	$k(T) = (1.22 \times 10^{-13})\exp(2767.85/T)$
2,4,5-TrBT + OH → IM17 via TS30	$k(T) = (1.38 \times 10^{-13})\exp(645.82/T)$
2,4,5-TrBT + OH → P14 + Br via TS31	$k(T) = (1.53 \times 10^{-13})\exp(2152.34/T)$

Table 2 The configuration parameters of polybromobenzenes

	$\log k_{OH}$	M.V	M.W	E_{HOMO}	E_{LUMO}	D.M	Q^+	Q^-	E
1,2,4,5-TEBB	-11.91009489	153.338	389.68899	-0.2897	-0.02807	0.0001	0.204016	-0.192677	-10517.95196
2,4,5-TrBT	-11.7721133	128.921	325.79413	-0.28273	-0.01628	1.8941	0.547654	-0.7213	-7985.800884
HBB	-12.24260397	192.222	545.51002	-0.29651	-0.05088	0.0001	0.078834	-0.08032	-15660.84901
PBEB	-12.0347983	205.352	495.63081	-0.28991	-0.03649	1.5466	0.321931	-0.60783	-13167.99394
PBT	-12.18976748	194.444	481.61516	-0.29022	-0.03685	1.4492	0.241936	-0.850464	-13128.69982
PeBB	-12.05650548	165.317	467.59951	-0.29311	-0.03857	0.605	0.206756	-0.24452	-13089.39986