

Formation of Polybrominated Dibenzo-*p*-dioxins/Furans (PBDDs/Fs) by the Pyrolysis of 2,4-Dibromophenol, 2,6-Dibromophenol, and 2,4,6-Tribromophenol

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This study examined the thermal reactions of 2,4-dibromophenol (diBP), 2,6-diBP and 2,4,6-triBP. The products obtained under pyrolytic conditions were analyzed by gas chromatography/mass spectrometry (GC/MS). 2,7-dibromodibenzo-*p*-dioxin (diBDD) was the major compound produced from the thermal reaction of 2,4-diBP. In addition, monoBDD and triBDDs were obtained through a process of debromination and bromination, respectively. The pyrolysis of 2,6-diBP and 2,4,6-triBP produced two major brominated dioxin isomers through direct condensation and a Smiles rearrangement. The two *ortho*-Brs in 2,6-diBP and 2,4,6-triBP mainly led to the production of dioxins, whereas in addition to 2,7-diBDD, 2,4-diBP produced two furans as minor products, 2,8-dibromodibenzofuran (diBDF) and 2,4,8-triBDF, through the intermediate dihydroxybiphenyl (DOHB). The maximum yield of the major dioxins was obtained at 400 °C, and decomposition by debromination at 500 °C resulted in less substituted bromodioxins.

Key Words : Pyrolysis, Bromophenol, GC/MS, Formation mechanism

Introduction

Various brominated compounds as alternatives to chlorinated compounds have been used in areas such as agriculture pesticides, pharmacy industries, flame retardants and other fine chemicals.^{1,2} Recently, there has been increasing concern regarding the formation of polybrominated dibenzo-*p*-dioxins and furans (PBDDs/Fs) during combustion and thermal processes due to the increased use of brominated materials.³⁻⁵ PBDDs/Fs also have been detected as impurities in brominated phenols (BPs) and brominated flame retardants (BFRs), with toxicities similar to those of polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs).^{6,7}

Two dominant mechanisms for the formation of PCDDs/Fs,⁸⁻¹⁰ a *de novo* synthesis and a reaction through various organic precursors, have also been suggested in the formation of PBDDs/Fs.¹¹⁻¹³ In incinerators, brominated aromatic compounds such as BPs and BFRs, which are used in specific plastics, are the major sources of the PBDDs/Fs that are formed through a precursor mechanism. Moreover, the yields of PBDDs/Fs from the precursors are higher than those of PCDDs/Fs due to the weaker bond strength of the C-Br bond compared with that of C-Cl.¹⁴⁻¹⁷

The precursor mechanism can be divided into two different intermediates depending on the position of the substituted Br on the phenol ring: brominated phenoxyphenol (POP) and dihydroxybiphenyl (DOHB). The BP containing *ortho*-bromine produces PBDDs *via* POP whereas *ortho*-hydrogen produces the PBDFs *via* DOHB.^{14,18,19} Some studies have reported the mechanism for the formation of PBDDs/Fs from various BFRs. However, considerably less research has been performed on the BPs despite they being more reactive precursors to PBDDs/Fs.^{20,21}

The reaction temperature is an important factor in the formation of PBDDs/Fs because it can determine the fate of the precursor, and the types of isomers produced. Borojovich and Aizenshtat¹⁹ reported the thermal behavior of various brominated compounds depending on the reaction time at a fixed temperature, 600 °C, under pyrolytic conditions. Although many products including PBDDs/Fs were observed, they did not identify the isomers. Sidhu *et al.*¹⁴ proposed reaction kinetic models for the formation of tetraCDD and tetraBDD from the pyrolysis of 2,4,6-triCP and 2,4,6-triBP, respectively, but only compared the reactivity of the trihalogenated phenols based on the bond strengths between the carbon and halogen.

This study examined the pyrolytic thermal behavior of 2,4-diBP, 2,6-diBP and 2,4,6-triBP over a reaction time of 10 min at temperatures ranging from 300 to 500 °C. The pyro-products were identified by gas chromatography/mass spectrometry and were compared with those from our previous study¹⁸ to confirm the type of PBDDs/Fs isomers. In addition, a formation mechanism of the pyro-products from each precursor over the temperature range is proposed based on the products identified.

Experimental Section

Chemicals and sample preparation. The 2,4-diBP, 2,6-diBP and 2,4,6-triBP with >99% purity were purchased from Aldrich (Milwaukee, WI, USA). All the solvents were of pesticide residue grade and obtained from J. T. Baker (Phillipsburg, NJ, USA). The reaction tubes (10 cm long, 5 mm ID) were prepared by sealing one end of borosilicate glass Pasteur pipettes. Approximately 0.5 mg of each bromophenol was inserted into a reaction tube, with both

ends packed with quartz wool. The tip of the reaction tube was sealed under air atmosphere and placed in a muffle furnace. The furnace temperature was initially set to 100 °C, and held at that temperature for 10 min. The reaction temperatures were 200, 300, 400, and 500 °C, and were held at each temperature for 10 min. After pyrolysis, the reaction tube was removed from the furnace and allowed to cool to ambient temperature. The glass tube was opened and the contents were extracted thoroughly with 10 mL of methylene chloride using an ultra-sonicator. The extract was concentrated to approximately 1 mL using a rotary evaporator. An aliquot of 1 μ L was injected sequentially into the GC/MS, as described below.

GC/MS. An Agilent GC/MS system, which consisted of an Agilent 6890 gas chromatograph and an Agilent 5973N mass spectrometer (Palo Alto, CA, USA) was used to confirm the products formed by the thermal gas phase reactions. The samples were injected in a split mode (10:1 ratio). The carrier gas was helium (99.999%), which was flowed at a rate of 1 mL/min and an average velocity of 37 cm/sec. The oven temperature was initially held at 80 °C for 5 min. It was then increased to 300 °C at 10 °C/min, and held at that temperature for 5 min. A DB-5MS cross-linked 5% phenyl methylsilicone fused-silica capillary column (30 m \times 0.25 mm I.D., 0.25 μ m film thickness) was used to separate the products. The column was interfaced directly to the electron impact (EI) ion source of the mass spectrometer. The ion source was operated at 70 eV. The injection port, transfer line and ion source temperature were set at 280, 280 and 230 °C, respectively.

Results and Discussion

Pyrolysis of 2,4-dibromophenol. A reaction of halogenated phenols through a precursor mechanism requires the elimination of a halogen or a hydrogen atoms, which combines with the carbon of the *ortho* position to produce PBDDs/Fs. 2,4-diBP, as a precursor, has a similar chemical structure to 2-bromophenol (2-BP) except for having an extra Br at the *para* position. Therefore, 2,4-diBP is expected to produce pyro-products analogous to 2-BP.

Figure 1 shows a total ion chromatogram (TIC) obtained

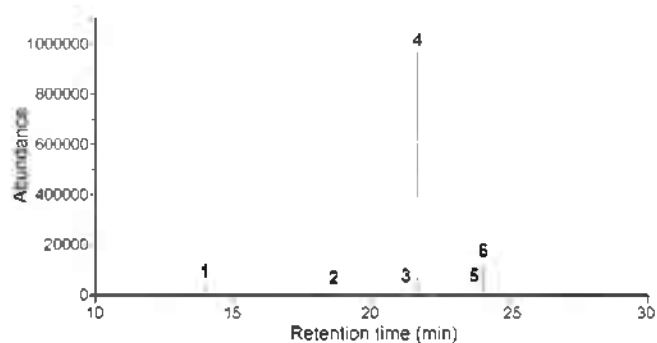


Figure 1. Total ion chromatogram of the pyro-products formed by the pyrolysis of 2,4-dibromophenol at 400 °C for 10 min: (1) tribromobenzene; (2) monobromodibenzo-*p*-dioxin; (3) 2,8-dibromodibenzofuran; (4) 2,7-dibromodibenzo-*p*-dioxin; (5) 2,4,8-tribromodibenzofuran; (6) 1,3,8-tribromodibenzo-*p*-dioxin.

from the pyrolysis of 2,4-diBP for 10 min at 400 °C. The most abundance product was identified as 2,7-dibromodibenzo-*p*-dioxin (diBDD) with a relative area of approximately 85%. A cluster of its molecular ion shows an isotope pattern of Br containing two Br atoms. Moreover, the characteristic ions have a typical dioxin structure, which indicates the fragment ions $[M-Br]^-$, $[M-COBr]^+$ and $[M-2COBr]^+$ as well as $[M]^{2-}$ (Table 1). The other minor brominated dioxins and furans observed on the TIC were also identified in a similar manner to that used to confirm the molecular structure of 2,7-diBDD. Tribromobenzene, which is a by-product arising from 2,4-diBP, was also confirmed with an abundance of approximately 3%.

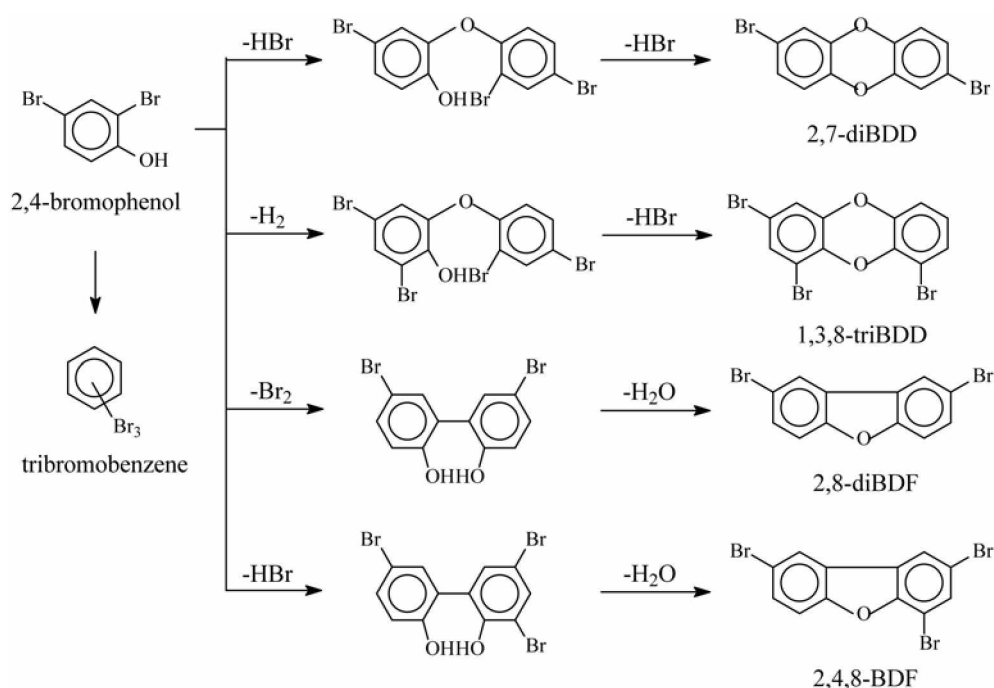
The isomer types of monoBDD and diBDD/F except triBDD/F were classified by comparing their retention times with those of the pyro-products of mono-BPs observed in a previous study.¹⁸ The isomers confirmed were 1-BDD, 2,8-diBDF and 2,7-diBDD, which helped determine the formation mechanism of PBDDs/Fs, as described below.

Generally, the formation of dioxins and furans are initiated by a loss of the phenoxy hydrogen of phenol. The leading mechanism for producing dioxins from a precursor involves the formation of *o*-phenoxyphenol (POP) as an intermediate due to the debromination of the *ortho* Br. 2,4-dibromophenoxy-4-bromophenol, which is formed from 2,4-diBP, pro-

Table 1. Retention times (RTs) and characteristic ions of the brominated dioxins and furans

| Compounds | RTs (min) | Characteristic ions and their <i>m/z</i> values |
|---------------------------|---------------------|---|
| <i>brominated dioxins</i> | | |
| monoBDD | 18.66 | 262 $[M]^-$, 184 $[M-Br]^-$, 155 $[M-COBr]^+$, 131 $[M]^{2+}$, 127 $[M-2CO-Br]^-$ |
| diBDDs | 21.51, 21.67 | 342 $[M]^-$, 261 $[M-Br]^-$, 233 $[M-COBr]^+$, 171 $[M]^{2+}$, 126 $[M-2COBr]^-$ |
| triBDDs | 23.93, 24.05 | 420 $[M]^-$, 342 $[M-Br]^-$, 313 $[M-COBr]^+$, 260 $[M-2Br]^-$, 210 $[M]^{2+}$, 204 $[M-2COBr]^-$ |
| tetraBDDs | 26.18, 26.31 | 500 $[M]^-$, 419 $[M-Br]^-$, 391 $[M-COBr]^+$, 340 $[M-2Br]^-$, 284 $[M-2COBr]^+$, 250 $[M]^{2-}$ |
| pentaBDDs | 28.83, 29.33, 29.56 | 577 $[M]^-$, 499 $[M-Br]^-$, 470 $[M-COBr]^+$, 420 $[M-2Br]^-$, 362 $[M-2COBr]^+$, 289 $[M]^{2-}$ |
| <i>brominated furans</i> | | |
| diBDF | 21.25 | 326 $[M]^-$, 246 $[M-Br]^-$, 217 $[M-COBr]^+$, 163 $[M]^{2+}$, 138 $[M-CO-2Br]^-$ |
| triBDF | 23.86 | 404 $[M]^-$, 326 $[M-Br]^-$, 297 $[M-COBr]^+$, 246 $[M-2Br]^-$, 216 $[M-CO-2Br]^+$, 202 $[M]^{2-}$, 137 $[M-CO-3Br]^+$ |

*Bold *m/z* values: base peaks.



Scheme 1. Formation pathways of the pyro-products of 2,4-dibromophenol.

ceeds to produce 2,7-diBDD through the elimination of HBr. Although Br in the *ortho*-position of phenol is easily eliminated to yield 2,7-diBDD, dehydrogenation in another *ortho*-position can also occur during the pyrolysis process, and 1,3,8-triBDD can be formed through a tetra brominated POP intermediate. Unlike POP, *o,o*-dihydroxybiphenyl (DOHB), which is an intermediate of PBDF, can be also formed although *ortho-ortho* carbon coupling requires a higher energy than that needed for the formation of POP. The condensation by removing the two Br atoms and HBr of the *ortho* position can produce 2,8-diBDF and 2,4,8-diBDF, respectively, through dehydration. However, 2,4,6,8-tetraBDF was not observed due to the difficulty in detaching the two

ortho-hydrogens. Scheme 1 gives a summary of the pathways of these precursor processes.

Figure 2 shows the pyrolytic fate of the main products as a function of the pyrolysis temperature. The amount of 2,4-diBP decreased rapidly with increasing temperature up to 400 °C (line graph in Fig. 2). Consequently, the amounts of both 2,7-diBDD and 1,3,8-triBDD increased with increasing temperature up to 400 °C, which was followed by a decrease due to thermal degradation of these dioxins at 500 °C. 2,4,8-triBDF with a small amount appears at 300 °C but disappears at higher temperatures. These observations suggest the favorable formation of PBDFs at low temperatures.

Pyrolysis of 2,6-dibromophenol. The types of compounds produced by the pyrolysis of 2,6-diBP are relatively simple compared with those produced by 2,4-diBP. As shown in Figure 3, all the products identified on the TIC are dioxin congeners and consist of a mono to triBDDs. At 400 °C, two diBDDs are the main products, which comprise of 88% of the total products. In the case of 2,6-diBP, the two Brs of the *ortho*-positions promote the formation of POP, and the 1,6-diBDD produced by direct condensation is easily observed. However, two diBDD isomers were separated by GC analysis. The other diBDD was searched and identified as 1,9-diBDD, whose formation was attributed to a Smiles rearrangement. The latter process occurs only when two Brs in the *ortho*-positions of phenol are combined (Scheme 2). The amount of 1,9-diBDD formed by the Smiles rearrangement is slightly less than that of 1,6-diBDD, which can be explained by the facts that the formation enthalpy of 1,6-diBDD is lower than that of 1,9-diBDD and that the Smiles rearrangement produces 1,6-diBDD and 1,9-diBDD.²² MonoBDD with an abundance of approximately 9% was identified as 1-BDD, based on a comparison with the

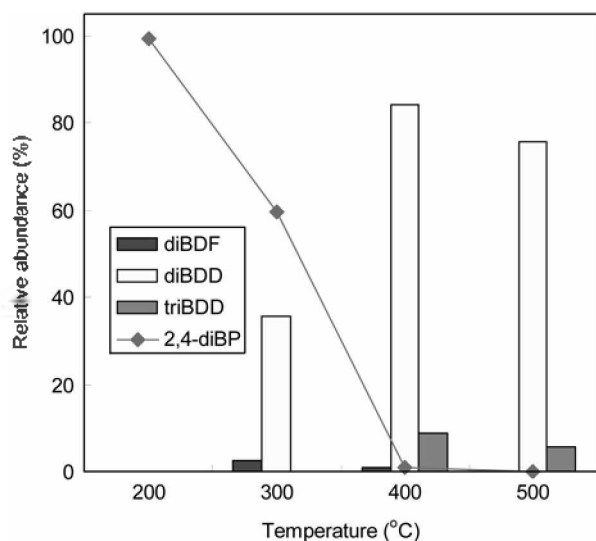


Figure 2. Thermal decay curve and formation of the pyro-products of 2,4-dibromophenol at different pyrolysis temperatures.

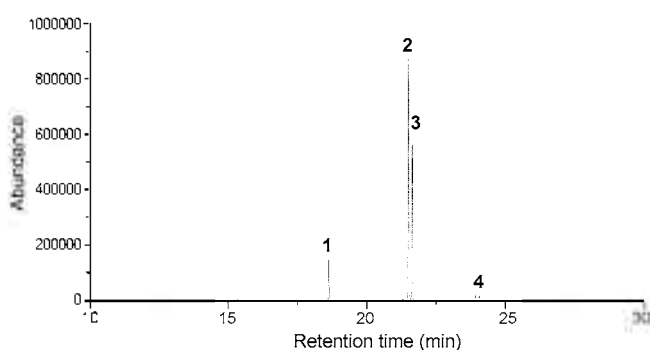


Figure 3. Total ion chromatogram of the pyro-products formed by the pyrolysis of 2,6-dibromophenol at 400 °C for 10 min: (1) 1-bromodibenzo-*p*-dioxin; (2) 1,6-dibromodibenzo-*p*-dioxin; (3) 1,9-dibromodibenzo-*p*-dioxin; (4) tribromodibenzo-*p*-dioxins.

retention time and the mass spectrum of the products obtained from the 2-BP pyrolysis in a previous study.¹⁸ Only 1-BDD is produced under the these pyrolytic conditions possibly by the debromination of both 1,6-diBDD and 1,9-diBDD. Although the amount of triBDDs was small, the two isomers were separated. The relative abundance of the two isomers was found to be similar to that of the diBDDs, which supports the explanation of the bromination of each diBDD. However, the two isomers of triBDDs were difficult to identify precisely due to the potential formation of too many isomers by bromination as well as the lack of authentic standard reagents.

Figure 4 shows the thermal decay curve and the formation of pyro-products of 2,6-diBP as a function of the pyrolysis temperature. The temperature dependent formation of diBDDs was similar to that of 2,4-diBP. Although the reaction rate of 2,6-diBP, as a function of the pyrolytic temperature, is slightly slower than that of 2,4-diBP, 2,6-diBP is entirely consumed to produce the dioxins at 400 °C. The complete reaction above 400 °C is considered to the result of the debromination or decomposition of dioxins. The debromi-

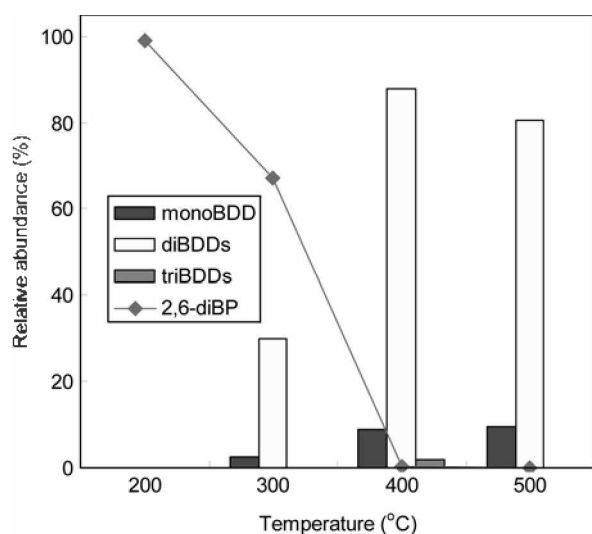


Figure 4. Thermal decay curve and formation of the pyro-products of 2,6-dibromophenol at different pyrolysis temperatures.

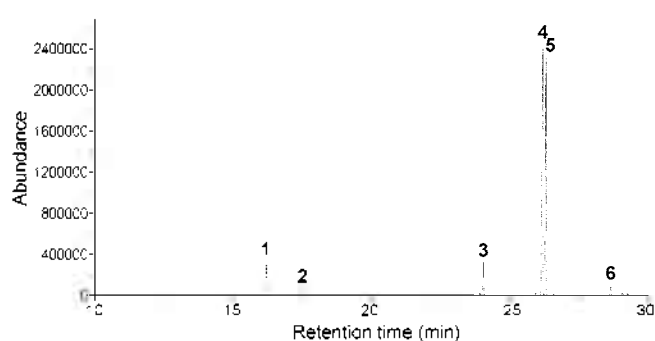
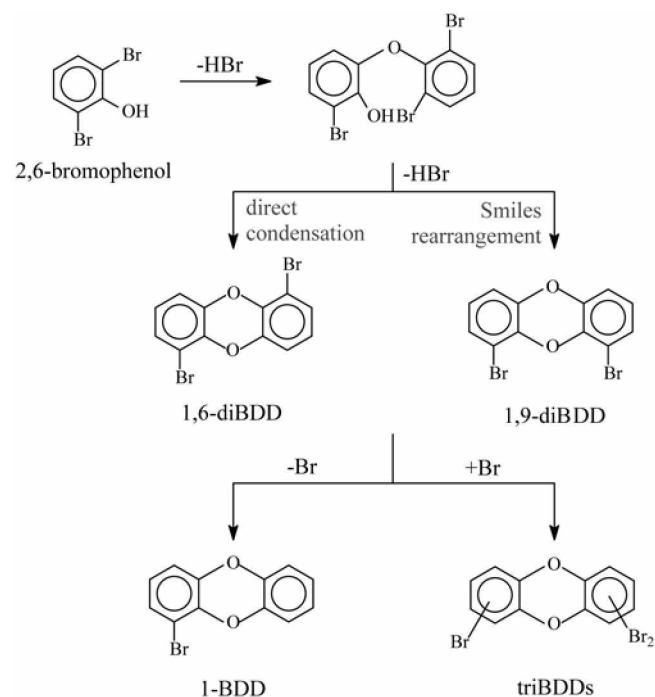


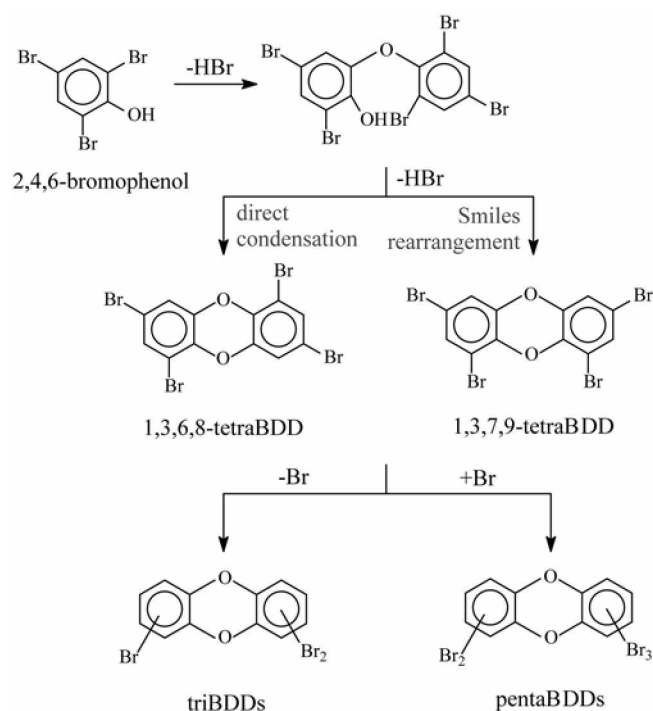
Figure 5. Total ion chromatogram of the pyro-products formed by the pyrolysis of 2,4,6-tribromophenol at 400 °C for 10 min: (1) 2,4,6-tribromophenol; (2) tetrabromobenzene; (3) 1,3,8-tribromodibenzodioxin; (4) 1,3,6,8-tetrabromodibenzodioxin; (5) 1,3,7,9-tetrabromodibenzodioxin; (6) pentabromodibenzodioxins.

nation is evidenced by the amount of monoBDD in the formation histogram: the relative concentration of the diBDDs decreases whereas that of the monoBDD increases at 500 °C. In addition, a small amount of triBDDs was observed at 400 °C. The triBDDs can be produced as a result of the addition of free Br radicals to diBDDs. These Br radicals were detached during the condensation of the precursor or the debromination of the dioxins.

Pyrolysis of 2,4,6-tribromophenol. Figure 5 shows the TIC obtained from the pyrolysis of 2,4,6-triBP at 400 °C. The compounds identified from the separated peaks are all brominated dioxins along with the unreacted precursor at that temperature. The most abundant products are tetraBDDs, whose relative abundance was 87% of the total products formed. Like 2,6-diBP, 2,4,6-triBP also produces two dioxin isomers through direct condensation and a



Scheme 2. Formation pathways of the pyro-products of 2,6-dibromophenol.



Scheme 3. Formation pathways of the pyro-products of 2,4,6-tribromophenol.

Smiles rearrangement. The direct condensation produces the 1,3,6,8-tetraBDD isomer only, whereas the Smiles rearrangement can produce 1,3,6,8- and 1,3,7,9-tetraBDD isomers (Scheme 3). These isomers were identified by the elution orders of a GC chromatogram on a non-polar column. In the case of chlorinated dioxins, the 1,3,6,8-tetraCDD isomer on the GC chromatogram was eluted earlier than 1,3,7,9-tetraCDD.²³ Therefore, peaks 4 and 5 on the TIC in Figure 5 were determined to be 1,3,6,8-tetraBDD and 1,3,7,9-tetraBDD, respectively.

During this thermal reaction, the triBDDs were presumably produced as a result of debromination. One of the triBDD isomers, corresponding to peak 3, coincides with 1,3,8-triBDD, which is probably produced through a dioxin formation mechanism from the pyrolysis of 2,4-diBP. This indicates that debromination occurs in the *peri* position of 1,3,6,8-tetraBDD, followed by the formation of 1,3,8-triBDD. The other triBDD isomer, 1,3,7-triBDD, can be formed by the removal of a Br from 1,3,7,9-tetraBDD. However, an authentic standard will be needed for precise identification due to the small peak abundance and ambiguous peak position. The three types of pentaBDDs could be explained by adding a Br to tetraBDDs although the amount was small. However, identifying the penta-BDDs is difficult because of many possible routes of adding Br to tetra-BDDs. Above 400 °C, the yields of tetraBDDs and pentaBDDs decrease gradually, whereas that of triBDDs increases. This observation supports the debromination process of tetraBDDs and pentaBDDs being the route for the formation of triBDDs.

The decay of 2,4,6-triBP was slightly slower than those of diBPs, resulting in low yields of tetraBDDs at 300 °C. This indicates that 2,4,6-triBP is not a very efficient precursor for

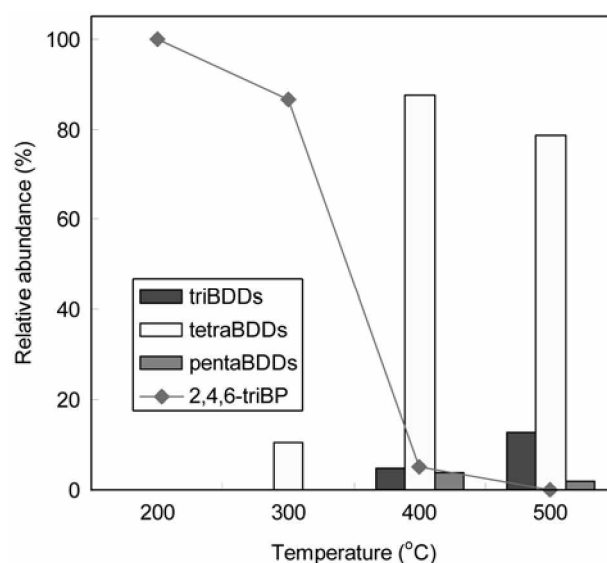


Figure 6. Thermal decay curve and formation of the pyro-products of 2,4,6-tribromophenol at different pyrolysis temperatures.

producing dioxins at low temperatures compared with other brominated phenols. Accordingly, 2,4,6-triBP is needed to produce brominated dioxins when the reaction temperature is > 300 °C.

Conclusion

The pyrolysis of 2,4-diBP, 2,6-diBP and 2,4,6-triBP leads to the production of brominated dioxins as the major products through the POP intermediate. In the case of 2,4-diBP, two brominated furans, 2,7-diBDF and 2,4,8-triBDF, *via* DOHB were observed albeit in small amounts. However, 2,6-diBP and 2,4,6-triBP, which have Br atoms at the two *ortho* positions, produced no furan compounds. The two Br atoms at the *ortho* positions of the precursors produced two dioxin isomers through direct condensation and a Smiles rearrangement. The minor products, tri and tetrabromobenzenes, were also produced as by-products of the precursors. The isomers of the pyro-products were not identified precisely due to the lack of commercially available authentic standards. However, some major products were identified by a comparison with their retention times and the mass spectra of the dioxins produced from the monoBPs in a previous study. The identification of these isomers provides information on the mechanism for the thermal reaction of brominated dioxins. The thermal study revealed the debromination of the major dioxins to occur above 400 °C. As a result, the relative amount of debrominated dioxin isomers increased whereas that of the major dioxins decreased.

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