Environ. Sci. Technol. **2003**, *37,* 5574−5580

Mechanisms of Dioxin Formation from the High-Temperature Pyrolysis of 2-Bromophenol

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Brominated hydrocarbons are the most commonly used flame retardants. Materials containing brominated hydrocarbons are frequently disposed in municipal and hazardous waste incinerators as well as being subjected to thermal reaction in accidental fires. This results in the potential for formation of brominated dioxins and other hazardous combustion byproducts. In contrast to chlorinated hydrocarbons, the reactions of brominated hydrocarbons have been studied only minimally. As a model brominated hydrocarbon that may form brominated dioxins, we studied the homogeneous, gas-phase pyrolytic thermal degradation of 2-bromophenol in a 1-cm i.d., fused-silica flow reactor at a concentration of 90 ppm, with a reaction time of 2.0 s, and over a temperature range of 300 to 1000 °C. Observed products included dibenzo-*p*-dioxin (DD), 1-monobromodibenzo-*p*-dioxin (1-MBDD), 4-monobromodibenzofuran (4-MBDF), dibenzofuran (DF), naphthalene, bromonaphthalene, 2,4- and 2,6-dibromophenol, phenol, bromobenzene, and benzene. These results are compared and contrasted with previous results reported for 2-chlorophenol. At temperatures lower than 700 °C, formation of 2-bromophenoxyl radical, which decomposes through CO elimination to form a bromocyclopentadienyl radical, forms naphthalene and 2-bromonaphthalene through radical recombination/rearrangement reactions. However, unlike the results for 2-chlorophenol, where naphthalene is the major product, DD becomes the major product for the pyrolysis of 2-bromophenol. The formation of DD and 1-MBDD are attributed to radical−radical reactions involving 2-bromophenoxyl radical with the carbon- (bromine) centered radical and the carbon- (hydrogen) centered radical mesomers of 2-bromophenoxyl radical, respectively. The potential product, 4,6-dibromodibenzofuran (4,6-DBDF) for which the analogous product, 4,6-dichlorodibenzofuran (4,6 DCDF), was observed in the oxidation of 2-chlorophenol, was not detected. This is attributed to the pyrolytic conditions of our experiments (e.g., shorter reaction times and higher temperatures) that favor reaction intermediates that form DD and 1-MBDD.

Introduction

Emissions of brominated hydrocarbons have been reported from various combustion sources (*1−6*). There has been a notable increase in everyday use of brominated flame retardants that will increase the quantity of brominated material reaching thermal waste treatment facilities (*4*). Materials containing brominated flame retardants and other brominated materials are also subject to accidental fires (*7*). Because the presence of bromine inhibits combustion, the conditions in these accidental fires will be sufficient to inhibit complete combustion, thus increasing the likelihood of formation of products of incomplete combustion (*7*). This results in increased concern over potential emissions of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs).

Chlorinated phenols are key intermediates in essentially all proposed pathways of formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (*8−12*). Similarly, brominated phenols and brominated flame retardants, e.g. polybrominated biphenyl ethers (PBDEs), have been identified as precursors to PBDD/Fs (*1, 4, 13−15*). More importantly, some studies have shown that brominated phenols may form more PBDD/Fs than the analogous chlorinated phenols form PCDD/Fs (*13, 16*). With this knowledge, it is interesting to note that the toxicity of the PBDD/Fs has been shown to be similar to the analogous PCDD/Fs (*17, 18*).

Previous work has also shown that the addition of bromine during combustion increases the production of PBDD/Fs, PCDD/Fs, and mixtures of brominated and chlorinated dibenzo-*p*-dioxins and dibenzofurans (*4, 19*). Some research suggests that bromination is 10 times more efficient than chlorination (*13*). This has been attributed to the predominant form of bromine being Br_2 versus HCl for chlorine (*4*). The addition of bromine may not only increase bromination but also increase chlorination, with the bromine serving as a good leaving group for displacement by chlorine (*4, 19−20*).

In this paper, we report the results of the study of 2-bromophenol as a model compound for the combustion of brominated hydrocarbons and a precursor for the formation of PBDD/Fs. The thermal degradation of 2-bromophenol was studied under pyrolytic conditions for a reaction time of 2.0 s over the temperature range of 300 to 1000 °C. These conditions are appropriate to formation in the post-flame zone of combustion systems. Our results complement and expand upon previously published studies of chlorinated and brominated phenols under slow-combustion conditions at lower temperatures and reaction times on the order of 10 to 100 seconds and 1 h as well as our previously published work on the pyrolysis of 2-chlorophenol (2-MCP) (*21−24*). Reaction pathways to PBDD/F products are proposed that are consistent with the experimental data. Pathways to non-PBDD/F products are also analyzed, and the intermediates in these pathways are discussed in relation to formation of PBDD/F and other pollutants.

Experimental Section

All experiments were performed using a high-temperature flow reactor system referred to in the archival literature as the system for thermal diagnostic studies (STDS). The detailed design has been published elsewhere (*25*). In short, the STDS consists of a high-temperature, 1-cm i.d. fused-silica flow reactor equipped with an in-line Varian Saturn 2000 GC/MS. The flow reactor is housed inside a furnace located inside a Varian GC where the temperatures surrounding the reactor are controlled. Pressure inside the reactor is also maintained at 1.00 ± 0.15 atm. Gas-phase products are cryogenically trapped at the head of the GC column in preparation for chemical analysis.

To maintain a constant concentration of 90 ppm, 2-monobromophenol (2-MBP)(Aldrich) was injected into a helium

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10.1021/es034387s CCC: $25.00

gas stream by a syringe pump through a vaporizer maintained at 280 °C. Gas-phase samples of 2-MBP then were swept by the helium flow through heated transfer lines (300 °C) into a 35-cm long, 1.0-cm i.d. fused-silica tubular flow reactor where the controlled high temperature was maintained from 300 to 1000 °C. The helium flow rate was varied with temperature so that the residence time inside the reactor was held at 2.0 s. The unreacted 2-MBP and the thermal degradation products were then swept through a heated transfer line to another Varian GC where they were cryogenically trapped at the head of a CP-Sil 8 phase capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness). To separate the individual reaction products, the column was temperature programmed from −60 to 300 °C at 15 °C/min. Detection and quantification of the products were obtained using a Varian Saturn mass spectrometer that was operated in the full-scan mode (40 to 650 amu) for the duration of the GC run.

Product concentrations (other than PBDD/Fs) were calculated based on the calibrations with standards of the products (Aldrich and Cambridge Isotope Lab) and the peak area counts from the chromatogram. Standards for PBDD/Fs with less than four bromines were not available. Concentrations of observed PBDD/Fs are reported based on calibrations for the analogous PCDD/F. This is a reasonably accurate approach as the peak area counts for various chlorinated and brominated aromatics and PCDD/Fs and PBDD/Fs were compared, and it was found that the difference in calibration factors for brominated aromatic hydrocarbons and chlorinated aromatic hydrocarbons varied less than 10%.

Only three chromatographic peaks were observed that were tentatively identified as PBDD/F based on their mass spectra: 1-bromodibenzo-*p*-dioxin, 4,6-dibromodibenzofuran, and 4-bromodibenzofuran. The mass spectral library match qualities for these species were 264, 326, and, 248, respectively. These products are the same three PBDD/Fs that were anticipated on the basis of predicted pathways from previous research on formation of PCDD/F from the analogous 2-chlorophenol (*24*). In the 2-chlorophenol study, the PCDD/F standards were available to confirm the identifications on the basis of GC retention time and mass spectral pattern. Although standards were not available to confirm the identifications with PBDD/F standards, we are confident in the assignments based on the combination of mechanistically anticipated product formation; comparison of GC retention times, mass spectral response, and mass spectral patterns of chlorinated and brominated hydrocarbons; and previous studies of the formation of PCDD/F from 2-chlorophenol (*24*).

The yields of the products were calculated using the following expression:

$$Y = \{[\text{Product}]/\ [\text{2-MBP}]_0\} \times 100$$

where [Product] is the concentration of the particular product formed (in moles) and $[\text{2-MBP}]_0$ is the initial concentration of 2-MBP (in moles) injected into the reactor. (Please note that in our previous publication on the pyrolysis of 2-chlorophenol (*24*) the concentration of the chlorinated products that contained two phenyl rings was multiplied by two. These products were dibenzo-*p*-dioxin, 4,6-dichlorodibenzofuran, 1-chlorodibenzo-*p*-dioxin, dibenzofuran, naphthalene, chloronaphthalene, and diphenylethyne.) Once the experimental procedure was fully developed, the repeatability of the experiments was within 10%.

The heats of reaction, ΔH_{rxn}, for key steps in product formation pathways were calculated using AM1, semiempirical molecular orbital formalism. The calculations were performed using the MOPAC computation program that is contained within the ChemBats3D Pro computer application. Without experimental benchmarks, the calculated ΔH_{rxn} cannot be considered to be completely accurate. They are shown to assess the likelihood of potential parallel pathways.

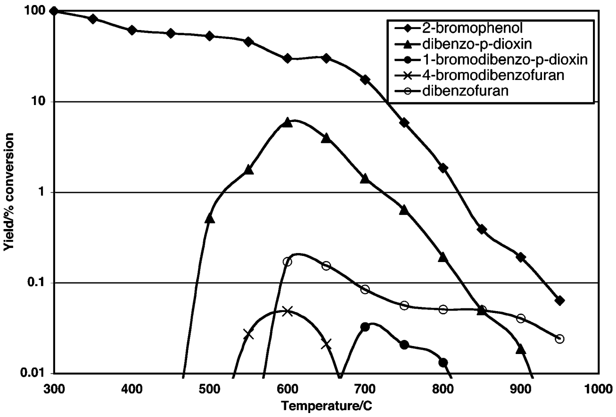


FIGURE 1. "Dioxin" products from the gas-phase pyrolysis of 2-MBP. $[\text{2-MBP}]_0 = 88$ ppm in helium. Gas-phase reaction time of 2.0 s.

Results

The temperature dependence of the thermal degradation of 2-MBP and the yield of "dioxin" products are presented in Figure 1 and Table 1 for a reaction time of 2.0 s. The nondioxin products are presented in Figure 2 and Table 1. Figures 1 and 2 are given on a semilogarithmic scale in which the percent yields of products (or percent of unconverted 2-MBP) are on a logarithmic scale versus temperature.

The thermal degradation of 2-MBP gradually increased from 300 to 650 °C, where the rate drastically accelerated, achieving 99% destruction at 850 °C.

Dibenzo-*p*-dioxin (DD), dibenzofuran (DF), 4-monobromodibenzofuran (4-MBDF), and 1-bromodibenzo-*p*-dioxin (1-MBDD) were observed between 500 and 900 °C. The anticipated product, 4,6-dibromodibenzofuran (4,6-DBDF) was not observed. Unlike DD and 4-MBDF, which were detectable at temperatures as low as 500 °C, significant yields of 1-MBDD were not observed until 700 °C with a maximum yield of 0.03%. The major product, DD, was observed between 500 and 900 °C with a maximum yield of 6% at 600 °C. The other dioxin products, DF and 4-MBDF, were detected at much lower yields with maximums of 0.17% and 0.05% at 600 °C, respectively. No brominated aromatics were detected above 950 °C.

Nondioxin products were also detected from the pyrolysis of 2-MBP (cf. Figure 2 and Table 1). Brominated products included bromobenzene (maximum yield of 0.04% at 750 °C), bromonaphthalene (maximum yield of 0.19% at 650 °C), 2,4-dibromophenol, and 2,6-dibromophenol (maximum yields of 0.06% and 0.05% at 650 °C, respectively). Other products included naphthalene, benzene, phenol, acenaphthalene, phenylethyne, and diphenylethyne.

Initially naphthalene and phenol were observed at 500 °C followed by 2,4-dibromophenol, 2,6-dibromophenol, and bromonaphthalene at 600 °C. However phenol and bromonaphthalene achieved their highest yields of 0.36% and 0.19% at 600 and 650 °C, respectively, whereas naphthalene achieved a maximum yield of 1.83% at 950 °C. All other products were not detected until 750 °C and reached their maximum yields at 900 °C.

Discussion

The formation of dioxin products (DD, 1-MBDD, 4-MBDF, and DF) indicates that stable phenoxyl radicals are formed in significant yields through loss of the hydroxyl-hydrogen. The formation of aromatics (phenol, bromobenzene, and benzene) indicates that simple substitution reactions are

TABLE 1. Percent Yield[a] of Products of Gas-Phase Pyrolysis of 2-Bromophenol

	temperature (°C)												
product	300	400	450	500	550	600	650	700	750	800	850	900	950
2-bromophenol	100	61.3	56.3	52.8	45.7	29.9	30.1	17.4	5.8	1.8	0.39	0.19	0.06
dibenzo-*p*-dioxin				0.52	1.78	5.96	3.97	1.42	0.64	0.19	0.05	0.02	
1-bromodibenzo-*p*-dioxin							0.003	0.03	0.02	0.01			
dibenzofuran						0.17	0.15	0.08	0.05	0.05	0.05	0.04	0.02
4-bromodibenzofuran					0.03	0.05	0.02						
naphthalene				0.02	0.03	0.04	0.07	0.36	0.71	1.15	1.35	1.44	1.83
bromonaphthalene						0.03	0.19	0.13	0.08	0.07	0.04	0.02	0.01
acenaphthalene									0.002	0.01	0.02	0.02	0.03
phenol				0.04	0.07	0.36	0.24	0.24	0.17				
2,4-dibromophenol					0.004	0.04	0.06	0.004					
2,6-dibromophenol						0.04	0.05	.003	0.001				
benzene									0.02	0.05	0.07	0.09	0.10
bromobenzene						0.02	0.03	0.03	0.04	0.03	0.006		
phenylethyne									0.01	0.02	0.03	0.05	0.03
diphenylethyne									0.04	0.15	0.19	0.10	

[a] Percent yield = {([Product])/[2-MBP]$_0$} × 100.

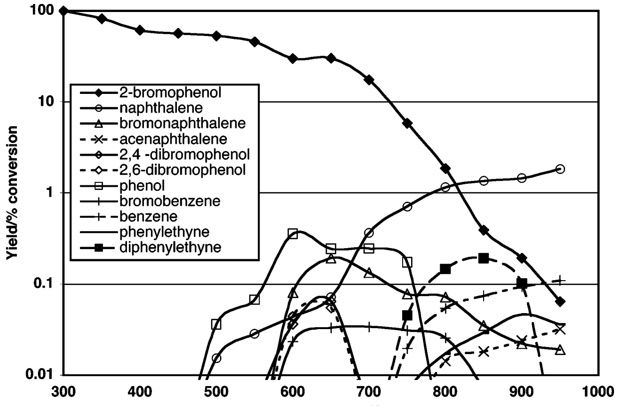


FIGURE 2. "Nondioxin" products from the gas-phase pyrolysis of 2-MBP. [2-MBP]$_0$ = 88 ppm in helium. Gas-phase reaction time of 2.0 s.

occurring. The formation of 2,4- and 2,6-dibromophenol is evidence of bromination of 2-MBP. The formation of larger aromatic molecules (naphthalene, acenaphthalene, and bromonaphthalene) is the result of molecular growth pathways that may involve smaller, even- or odd-numbered radicals. The formation of phenylethyne and diphenylethyne indicates fragmentation of the aromatic ring and reactions of even-numbered radicals.

2-MBP Decomposition. The decomposition of 2-MBP is initiated by loss of the phenoxyl hydrogen by unimolecular, bimolecular, or possibly other low energy pathways (including heterogeneous reactions). Unimolecular decomposition of the oxygen−hydrogen bond (reaction 1) is rapid. Our AM1 semiempirical molecular orbital calculations yield a heat of reaction of 79 kcal/mol.

$$C_6H_4BrOH \rightarrow C_6H_4BrO^\bullet + H^\bullet \qquad \Delta H_{rxn} = 79\ \text{kcal/mol} \quad \text{(Reaction 1)}$$

This is consistent with the activation energy for the reported rate coefficient for decomposition phenol, k_{phenol} (430−930 °C) = $3.2 \times 10^{15}\exp(-86\,500/RT)$ s^{-1} (**26, 27**), and the suggestion that the activation energy is 5 kcal lower for the reaction of 2,4,6-trichlorophenol than phenol (*28*). Studies have also shown that the O−H bond in 2-MBP is 0.10 kcal/mol weaker than the O−H bondin 2-MCP, and therefore H elimination is expected to be faster for 2-MBP than for 2-MCP (*29*).

Bimolecular propagation reactions under pyrolytic conditions include attack by H$^\bullet$ and Br$^\bullet$. On the basis of AM1 semiempirical molecular orbital calculations, thermodynamically feasible reactions of H$^\bullet$ include: phenoxyl hydrogen abstraction (reaction 2), bromine abstraction (reaction 3), bromine displacement (reaction 4), and hydroxyl displacement (reaction 5). Aromatic hydrogen abstraction is thermodynamically unfavorable. The AM1 calculated ΔH_{rxn} values shown are not precise and are given here for comparison purposes only.

$$C_6H_4BrOH + H^\bullet \rightarrow C_6H_4BrO^\bullet + H_2 \qquad \Delta H_{rxn} = -23\ \text{kcal/mol} \quad \text{(Reaction 2)}$$

$$C_6H_4BrOH + H^\bullet \rightarrow {}^\bullet C_6H_4OH + HBr \qquad \Delta H_{rxn} = -11\ \text{kcal/mol} \quad \text{(Reaction 3)}$$

$$C_6H_4BrOH + H^\bullet \rightarrow C_6H_5OH + Br^\bullet \qquad \Delta H_{rxn} = -29\ \text{kcal/mol} \quad \text{(Reaction 4)}$$

$$C_6H_4BrOH + H^\bullet \rightarrow C_6H_5Br + {}^\bullet OH \qquad \Delta H_{rxn} = 2\ \text{kcal/mol} \quad \text{(Reaction 5)}$$

Bromine atoms can also abstract phenoxyl hydrogens (cf. reaction 6). In contrast, the abstraction of an aromatic hydrogen by bromine (reaction 7) for comparison to the analogous chlorine reaction, vide infra) (*24*), abstraction of bromine by bromine, displacement of hydrogen by bromine, and displacement of hydroxyl by bromine are highly endothermic and unfavorable.

$$C_6H_4BrOH + Br^\bullet \rightarrow C_6H_4BrO^\bullet + HBr \qquad \Delta H_{rxn} = -8\ \text{kcal/mol} \quad \text{(Reaction 6)}$$

$$C_6H_4BrOH + Br^\bullet \rightarrow {}^\bullet C_6H_3BrOH + HBr \qquad \Delta H_{rxn} = 19\ \text{kcal/mol} \quad \text{(Reaction 7)}$$

Rate coefficients based on analogous reactions with phenol for reactions 2, 3, 4, and 6 are k_2 (730−880 °C) = $1.15 \times 10^{14}\exp(-12\,400/RT)$ cm^3/mol/s (*30*), k_3 (800−1010 °C) = $1.0 \times 10^{13}\exp(-11\,300/RT)$ cm^3/mol/s (*31*), k_4 (800−1010 °C) = $1.5 \times 10^{13}\exp(-7500/RT)$ cm^3/mol/s (*31*), and k_6 (25 °C) = 1.43×10^{14} cm^3/mol/s (*30*), respectively. No previous kinetic data was found for reaction 5. However, because of the very low endothermicity of the reaction, it cannot be ruled out as a decomposition pathway.

On the basis of the experimentally determined product formation, the dominant initiation pathways appear to be formation of 2-bromophenoxyl radical via reaction 1 (with some contribution from reactions 2 and 6) and formation of phenol via reaction 4. Reaction 4 is significant for 2-MBP and is faster than the analogous chlorine displacement in 2-MCP because of the weaker carbon−bromine (80.5 kcal/mol) versus carbon−chlorine (95.7 kcal/mol) bond (*20*). The ΔH_{rxn} for reaction 3 (−11 kcal/mol) is similar to that for the analogous reaction of 2-MCP (−14 kcal/mol). Reaction 7, hydrogen abstraction by a halogen atom, was found to be thermoneutral for 2-MCP and significantly endothermic and unfavorable for 2-MBP. Aromatic hydrogen atom abstractions by bromine atoms are not likely to play a role in the combustion chemistry of brominated hydrocarbons, as the resulting HBr is not highly stable.

Because of the low activation energies for reaction of 2-MBP, the purely gas-phase reactions described above can account for all the decomposition of 2-MBP above 750 °C. However, the initiation of 2-MBP decomposition at temperatures as low as 400 °C requires us to consider other possible low-energy initiation pathways. Heterogeneous wall reactions may result in a wall-collision-assisted reaction analogous to reaction 1. Trace impurities may also result in low-temperature decomposition. The potential contribution of these reactions have been previously analyzed for the oxidation of 2,4,6-trichlorophenol and been shown to not significantly impact subsequent propagation reactions (*32*).

Formation of Phenol, Bromobenzene, Benzene, Dibromophenol, Phenylethyne, and Diphenylethyne. On the basis of the early onset of phenol formation at temperatures as low as 500 °C, the dominant source of phenol in our study is probably the exothermic displacement of bromine by $H^{\bullet}$ (reaction 4). Higher yields of phenol are observed and at lower temperatures for 2-MBP than 2-MCP (*24*). This is a result of the lower activation energy for bromine displacement than chorine displacement.

Formation of bromobenzene occurs at much lower yields and higher temperatures than formation of phenol. This is consistent with the more endothermic displacements of the hydroxyl group by $H^{\bullet}$ to form bromobenzene (reaction 5) than the displacement of $Br^{\bullet}$ to form phenol. Benzene is formed in low yields and relatively high temperatures due to the endothermic displacement of the hydroxyl group by $H^{\bullet}$ from phenol ($\Delta H_{\mathrm{rxn}} = 4$ kcal/mol).

It is also notable that bromobenzene is initially produced at 600 °C while benzene is not formed until 750 °C. Bromobenzene is formed from 2-MBP at lower temperatures than chlorobenzene is formed from 2-MCP (*24*). This is in part attributable to the earlier onset of decomposition of 2-MBP than 2-MCP; however, bromine (versus chlorine) substitution may also facilitate OH displacement.

2,4-Dibromophenol and 2,6-dibromophenol form from the bromination of 2-MBP. Previous research suggests that bromine predominantly exists as Br_2 whereas chlorine is mainly found as HCl (*4*). With the excess Br_2, bromination can occur more readily than chlorination. It has also been noted that bromination is 10 times more efficient that chlorination (*13*). Thus, the evidence of bromination for 2-MBP is acceptable even though chlorination of 2-MCP was not evident in our previous study (*24*).

Considering the relatively high temperatures (725−875 °C) for formation of benzene and bromobenzene, and the formation of phenylethyne and diphenylethyne in the same temperature range, it is evident that 2-MBP fragments into primarily C2 radicals (vinyl and ethynyl) and C2 molecules (ethylene and acetylene). Molecular growth pathways resulting in formation of benzene and substituted benzene involving C2 units are well documented in the literature (*32*−*35*).

Formation of Naphthalene, Bromonaphthalene, and Acenaphthalene. Formation of polycyclics such as naphthalene, bromonaphthalene, and acenaphthalene are traditionally ascribed to molecular growth pathways involving largely C2 fragments (*32*−*35*). However, the low-temperature onset of formation of naphthalene (475 °C) suggests a pathway that does not require the complete fragmentation of 2-MBP and that is instead initiated at low temperatures.

Recently, resonantly stabilized cyclopentadienyl radicals have been recognized as potential precursors in the formation of naphthalene (*36*, *37*). We have already discussed how 2-MBP initially decomposes to 2-bromophenoxyl radical. It is well documented that the thermal decomposition of a phenoxyl radical expels CO to form a cyclopentadienyl radical with a reported rate coefficient of k_8 (730−1300 °C) $= 1 \times 10^{11.4}\exp(-22\,100 \pm 450/T)\ \mathrm{s}^{-1}$ and a ΔH_{f} of 20 kcal/mol (*27*, *38*). We believe that a similar elimination of CO from 2-bromophenoxyl radical forms bromocyclopentadienyl radical (reaction 8) as follows:

$$C_6H_4BrO^{\bullet} \rightarrow c{-}C_5H_4Br^{\bullet} + CO \quad \text{(Reaction 8)}$$

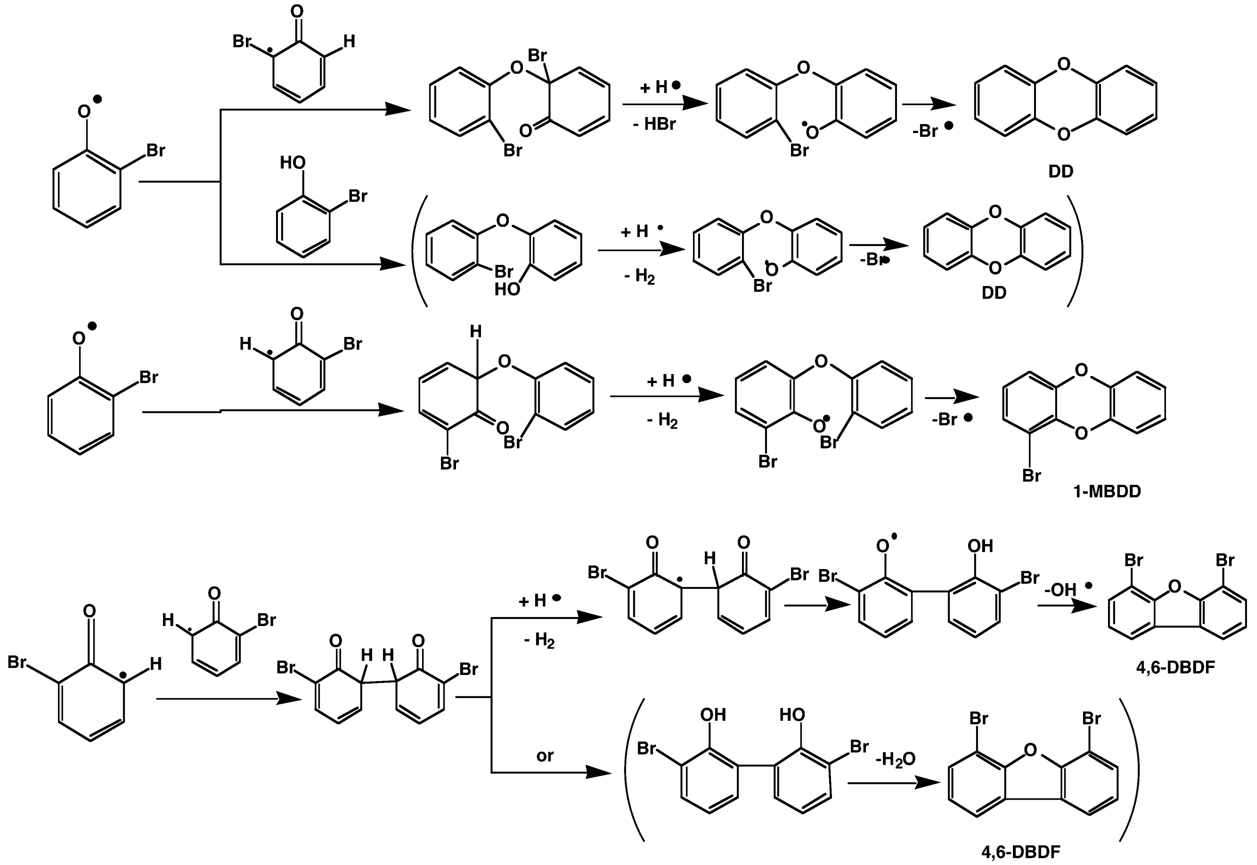
Recombination of two 2-bromocyclopentadienyl radicals, followed by rearrangement and $H^{\bullet}$ or $Br^{\bullet}$ elimination can result in formation of naphthalene if two $Br^{\bullet}$ are eliminated, formation of bromonaphthalene if one $Br^{\bullet}$ and one $H^{\bullet}$ are eliminated, and formation of dibromonaphthalene if two $H^{\bullet}$ are eliminated. The reported ΔH_{rxn} for the overall hydrocarbon reaction is 9.23 kcal/mol (*36*). The dominance of naphthalene, lower concentration of bromonaphthalene, and absence of dibromonaphthalene suggest that $Br^{\bullet}$ elimination is favored as would be expected considering the lower carbon−bromine bond strength and thermochemistry (*20*). This result also suggests that brominated hydrocarbons may undergo this type of molecular growth reaction more readily than hydrocarbons due to the more favorable elimination of bromine than hydrogen atoms. The formation of naphthalene was similar for both 2-MBP and our previous studies with 2-MCP (*24*). However, chloronaphthalene is formed in greater yields than bromonaphthalene (*24*). This is consistent with the elimination of bromine being much faster than that of chlorine as suggested by the weaker carbon−bromine versus carbon−chorine bond (*20*).

Acenaphthalene is formed in lower yields than naphthalene or bromonaphthalene at higher temperatures when benzene, phenylethyne, and diphenylethyne are also formed. This suggests that acenaphthalene is formed by traditional C2 molecular growth pathways where 2-MBP is completely fragmented.

Formation of Dibenzo-*p*-dioxin, 1-Bromodibenzo-*p*-dioxin, 4-Bromodibenzofuran, and Dibenzofuran. As expected, DD and 1-MBDD were formed. The anticipated product, 4,6-DBDF, was not observed. However, 4-MBDF and unbrominated DF were formed.

It is notable that DF forms at higher temperatures than DD and 1-MBDF. It also forms as phenol begins to decompose. Thus, we believe that DF is a recombination of unbrominated phenoxyl radical formed from decomposition of phenol (*39*). Essentially, the phenoxyl radical converts to the keto-mesomer that then recombines with another keto-mesomer to form a diketo-dimer. Single proton tautomerization followed by displacement of a hydroxyl radical forms DF. Alternatively, double tautomerization converts the diketo-dimer to the dihydroxy biphenyl (DHB)-dimer which can them eliminate water to form DF. Interestingly, the formation of DF from 2-MBP occurs at lower temperatures (600 °C) than from 2-MCP (700 °C). The $Br^{\bullet}$ concentration in the 2-MBP system is higher than the $Cl^{\bullet}$ concentration in the 2-MCP system due to the decomposition temperature of Br_2 being lower than that of HCl (*4*). The higher $Br^{\bullet}$ concentration leads to faster rates of hydrogen abstraction and DF formation. The yields of DF for both 2-MCP and 2-MBP are the

SCHEME 1. Postulated Pathways for the Formation of DD, 1-MBDD, and 4,6-DBDF



same, lending further evidence that they are formed by the same reaction pathway from the unhalogenated phenoxy radical, but with different rates as discussed above.

Comparison of DD and 1-MBDD formation from 2-MBP with previous results for 2-MCP suggest that they are formed directly from the brominated phenoxyl radical of 2-MBP (*24*). Scheme 1 depicts possible reaction pathways to DD, 1-MBDD, and 4,6-DBDF from the reaction of the different mesomers of 2-bromophenoxyl radical. The pathways are analogous to the pathways suggested for 2-MCP (*24*).

In the uppermost pathway, the oxygen-centered radical mesomer recombines with the carbon- (bromine) centered radical mesomer to form a keto-ether. Following the abstraction of bromine by $H^{\bullet}$, DD is formed by intra-annular elimination of $Br^{\bullet}$.

Another possible pathway for the formation of DD is through a radical−molecule reaction shown in parentheses below the radical−radical pathway in Scheme 1. This reaction depicts the oxygen-centered radical mesomer reacting with 2-MBP via $Br^{\bullet}$ displacement to form a bromohydroxy diphenyl ether (HDE) followed by the abstraction of hydrogen by $H^{\bullet}$. DD is then formed by intra-annular displacement of bromine. It has been previously suggested that this radical−molecule reaction is too slow to account for the observed yields of DD from 2-MCP (*32*).

Formation of 1-MBDD, shown as the third pathway in Scheme 1, is initiated by the recombination of the oxygen-centered radical mesomer and the carbon- (hydrogen) centered radical mesomer to form a keto-ether. Following loss of hydrogen to form the phenoxyl diphenyl ether (PDE), ring closure to form 1-MBDD occurs through intra-annular displacement of $Br^{\bullet}$.

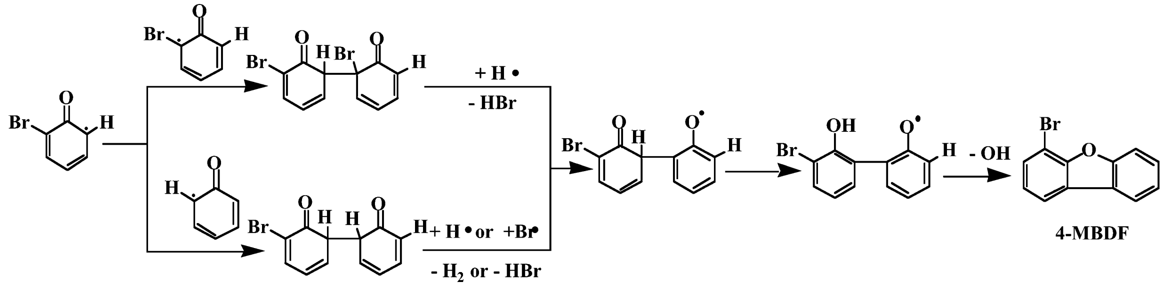
The last two pathways in Scheme 1 depict the possible pathways to formation of 4,6-DBDF. Initially for both pathways, two carbon- (hydrogen) centered radical mesomers react to form the diketo-dimer. The dimer can then react via the upper pathway through abstraction of hydrogen by $H^{\bullet}$, followed by tautomerization and displacement of the hydroxyl group to form 4,6-DBDF. An additional possibility is the lower pathway where the diketo-dimer double tautomerizes and then eliminates H_2O to from 4,6-DBDF.

The lack of formation of 4,6-DBDF could be considered surprising considering previous studies in the literature that reported dibenzofuran as the preferred product of reaction of unchlorinated phenoxyl radicals through the carbon-centered radical mesomer and chlorinated dibenzofurans as the preferred product from the reaction of various chlorinated phenols under *oxidative* conditions (*21−22, 40−42*). In these studies, the observed formation of dibenzofurans as the dominant product was justified on the basis that the carbon-centered radical mesomer, which leads to the dibenzofuran, was more stable than the oxygen-centered mesomer (*39*). However, in our previous study of 2-MCP, we noted that 4,6-DCDF was not formed (*24*). A previous study of the pyrolysis of 2-MBP for a reaction time of 1 h, reported DD as the main product at 600 °C without report of 4,6-DBDF as a product (*23*).

We believe that under pyrolytic conditions, the abstraction of hydrogen by $H^{\bullet}$ to form 4,6-DBDF is slower than the abstraction of bromine by $H^{\bullet}$ to form DD. This is in contrast to oxidative conditions where the hydroxyl radical should rapidly abstract hydrogen and form 4,6-DBDF or 4,6-DCDF from 2-MBP or 2-MCP, respectively (*21−22, 40−42*).

On the basis of all past and present results, it appears that oxidative conditions favor 4,6-DBDF formation, whereas pyrolysis favors DD formation (*21−24, 40−42*). It is also notable that the maximum yield for DD formation from 2-MBP is 20× higher than for 2-MCP. This is reasonable because the ΔH_{rxn} for the second displacement of Br to form

SCHEME 2. Proposed Pathways for Formation of 4-MBDF



DD is exothermic (−12 kcal/mol) and the ΔH_{rxn} displacement of Cl is endothermic (11 kcal/mol), resulting in formation of DD being more favorable for 2-MBP.

1-MBDD had slightly lower yields but occurred over the same temperature range as formation of 1-MCDD from 2-MCP. Clearly, 2-MBP and 2-MCP undergo very similar formation mechanisms with the halogen having little effect on the formation of the product. This suggests that the radical−radical recombination step is rate limiting, rather than the ring closure by halogen displacement. The slightly lower yield of 1-MBDD versus 1-MCDD may be due to competition with formation of DD. Ab initio molecular orbital calculations are under way to determine how bromine and chlorine affect the resonance structure of the halogenated phenoxyl radical.

4-MBDF was the only product formed for which the chlorinated analogue was not observed in our study of 2-MCP. Scheme 2 depicts reasonable pathways for the formation of 4-MBDF. Two pathways are depicted: (1) the carbon-(hydrogen) centered radical mesomer can recombine with the carbon- (bromine) centered radical mesomer; or (2) the carbon- (hydrogen) centered radical mesomer can recombine with an unbrominated carbon-centered phenoxyl radical to form a diketo-dimer. For the first pathway, $H^{\bullet}$ abstracts bromine and, in the second, $H^{\bullet}$ abstracts another hydrogen. Both pathways then undergo tautomerization followed by displacement of hydroxyl to form 4-MBDF. On the basis of comparisons to simple alkane reactions for the abstraction of bromine by $H^{\bullet}$ and the abstraction of hydrogen by $H^{\bullet}$, the upper pathway is a much more favorable route for the 4-MBDF formation (*43*−*45*).

In summary, we have proposed reasonable mechanisms for the formation of each observed product of the pyrolysis of 2-MBP. Reaction kinetic models that will be needed to better understand the competition between molecular growth pathways to form PAH and the relative yield of bromine-substituted dibenzo-*p*-dioxin products and bromine-substituted dibenzofuran products are under development. These results, mechanisms, and reaction kinetic codes can serve as a model for the formation of PBDD and PBDF from the range of brominated phenols present in full-scale combustors and help to decipher the origin of PBDD/F fingerprints that can be used to identify the specific sources of PBDD/F in the environment.

The results of this study clearly suggest an increased propensity for dioxin and furan formation from brominated precursors, viz. The maximum yield of DD alone was 20 times higher for 2-MBP than for 2-MCP (*24*). The continued used of brominated flame retardants that may be disposed in incinerators and energy recovery devices as well as accidental fires in which brominated chemicals are present, suggests that additional attention should be paid to PBDD/F formation from combustion of brominated chemicals.

Acknowledgments

We gratefully acknowledge the assistance of our colleagues, Dr. Lavrent Khachatryan and Alexander Burcat, in evaluation of the thermochemistry presented in this manuscript as well as helpful discussions concerning the mechanisms of dioxin formation. We acknowledge the partial support of this work under EPA cooperative agreement CR 827030 with Dr. Paul Lemieux as well as the Patrick F. Taylor Chair foundation.

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Received for review April 24, 2003. Revised manuscript received August 15, 2003. Accepted September 17, 2003.

ES034387S