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Kinetics of Toxic Combustion By-Product Formation During Brominated Flame Retardant Incineration

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Brominated flame retardants have been widely used in the textile and plastics industry for many years. Some concern has been raised with regard to the toxicity of brominated flame retardants such as polybrominated biphenyls (PBBs)[1]. Testing of PBBs indicates they may be as toxic as their chlorinated counterparts (i.e., polychlorinated biphenyls (PCBs))[2]. Most recently, companies involved in the production of these materials are investigating methods for disposing both production waste products and outdated flame retardant materials. High temperature incineration is one method being considered for the disposal of brominated materials; consequently, the combustion and thermal degradation properties of these materials is of great interest.

Analyses of PBBs and polybrominated diphenyl ethers (PBDPEs) have been widely reported in the literature[3-6]. In these studies, various industrial mixtures and pure components of brominated flame retardants were characterized with respect to their chromatographic properties, composition, and purity. The thermolysis of PBDPEs has recently been reported[7]. These compounds produced a host of polybrominated dibenzofurans (PBDFs) and polybrominated dibenzodioxins (PBDDs). Condensed phase work was also conducted by other researchers using open quartz tubes[8]. PBDFs and PBDDs were observed to form in extremely high yields from 2,4,6-tribromophenol (2,4,6-TBP), tetrabromobiphenol A, and pentabromophenol (up to 89.6% yields) with maximum formation at 800°C. PBDFs and PBDDs have also been observed in similar studies of the thermal degradation of industrial mixtures such as Bromkal-70-DE, Bromkal-70-5-DE, Bromkal-G1, FR 300 BA, and Firemaster BP-6[4].

In 1990, our lab reported the results of the first known controlled, gas phase thermal decomposition of three polybrominated flame retardant materials[9]. These materials, 2,4,6-TBP, 1,2-bis-(tribromophenoxy) ethane (bis-TBPA), and a mixture of PBDPEs were studied in a high temperature flow reactor system. Both oxidation and pyrolysis behavior were studied for a 2 sec gas phase residence time over a temperature range of 300 to 800°C. Although each sample was relatively thermally fragile, measurable quantities of brominated organic products of potential environmental concern was observed.

Major organic products observed from 2,4,6-TBP were dibromophenol (pyrolysis) and tetra-bromodibenzo-p-dioxin (tetra-PBDD) (oxidation). In air, tribromophenoxy ethene and two tetra-BDD isomers were formed from 1,2 bis-TBPA, while only one dibromophenol isomer was observed in the nitrogen. The PBDE mixture resulted in the formation of various brominated benzenes, brominated alkanes, and brominated alkenes, as well as several isomers of PBDDs and PBDFs. The greatest yields (~5%) of PBDDs and PBDFs were observed from 1,2 bis-TBPE mixture. The yields of products were calculated with the assumption that detector response for the product is the same as for the parent. Thus, the data must be considered to be semi-quantitative because of the lack of appropriate calibration standards.

Although each test material has the tribromophenoxy ($C_6H_3Br_3O$) functional group incorporated into its molecular structure, the nature of the links to the remaining atoms and groups play a large role in the material's destruction and product formation. However, because of space limitation, this paper only discusses a model compound (i.e., 2,4,6-TBP).

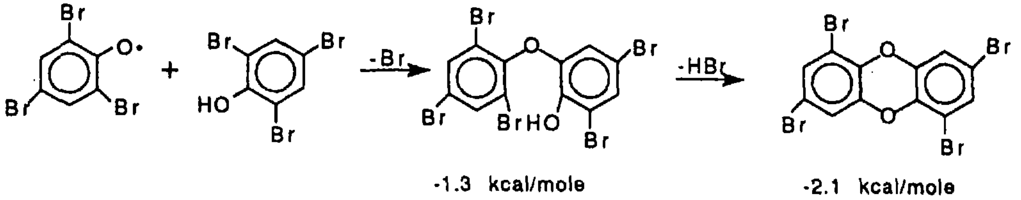
It was observed that 2,4,6-TBP decomposes much more rapidly in air than in nitrogen atmosphere. Using group additivity, the heat of formation (ΔH_f), entropy (S), and heat capacity at 1000°C (Cp) were calculated to be -6.7 kcal/mole, 106.8 cal/deg mole, and 61.8 cal/deg mole, respectively[10]. Still, the strengths of the various bonds are not directly calculable because the thermodynamic properties of the resultant product radicals are not known. However, the phenolic hydrogen is expected to be the most weakly bonded hydrogen (the bond dissociation energy (D_o) in phenols is 86.5 kcal[11]). The weakest bond in the molecule is clearly the carbon-bromine bond, which has a D_o of 78 kcal/mole in bromobenzene[11]. The presence of additional bromines is expected to further weaken these bonds.

As a result, abstraction of the phenolic hydrogen by oxygen atoms or hydroxyl radicals is expected to be the main decomposition route under oxidative conditions, since abstraction of bromine forms only weak O-Br or OH-Br bonds. The resulting phenoxy-type radical is expected to rapidly decompose through the expulsion of carbon monoxide (CO) in a mechanism similar to that previously proposed for benzene[12]. The resulting short-lived intermediate products (e.g., tribromocyclopentadiene) were observed in out experiments[9].

Displacement of bromine by hydrogen atoms is probably the preferred mechanism of destruction under pyrolytic conditions. Displacement of the functional group from the benzene ring has been previously shown to be the preferred mode of attack for various substituted benzenes (chlorobenzenes), toluene, and aniline.[13-15] The formation of dibromophenol as the only major reaction product[9] in nitrogen is evidence for this mechanism.

Tetra-PBDDs were observed from 2,4,6-TBP in oxidative conditions. The observed yields of PBDDs appear to be greater then those previously observed for polychlorinated dibenzo-p-dioxins (PCDDs) yields from the PCB precursors in studies conducted using the same experimental apparatus[16]. Thus, the mechanism of their formation is of key environmental concern.

In the formation of tetra-PBDD from 2,4,6-TBP, the initial step must involve the addition of the tribromophenoxy radical to 2,4,6-TBP through displacement of a bromine atom, hydrogen atom, oxygen atom, or hydroxyl radical. Displacement of the hydroxyl group by a phenoxy radical is exothermic, but removes the oxygen necessary for further reactions to form PBDDs. Displacement of bromine from 2,4,6-TBP by tribromophenoxy is expected to be nearly thermoneutral ($\Delta H_f = 1.3$, in the analogous phenoxy-bromobenzene reaction). Hydrogen atom displacement by phenoxy radical is highly endothermic. Thus, displacement of bromine is preferred "dimerization" step and the resulting ring closure by HBr elimination is exothermic (cf. Rxn 1):



(Rxn 1

Only one tetra-PBDD (the 1,3,6,8 isomer) can be formed from the symmetrical 2,4,6 TBP by this mechanism.

To model our data[9] we modified the model of Shaub and Tsang that was developed for formation of PCDDs from chlorophenols[17]. Changes to Shaub and Tsang mechanism are given in Table 1 and the results obtained using this modified mechanism are given in Table 2. The PBDD yields obtained from kinetic modeling agreed well with our experimental values. This is in contrast to the PCDD formation results which grossly underpredict observed experimental yields. These latter results have been used to suggest that surface reactions must be responsible for PCDD formation. Both the experimental results and the modeling results gave greater yields of PBDDs than PCDDs for experiments performed under similar conditions. These higher PBDDs yields can be attributed to the weak phenyl bromine bonds which facilitate displacement of bromine by phenoxy radicals, hydroxyl radicals, and oxygen atoms. Interestingly displacement of chlorine from chlorobenzene by a phenoxy radical is endothermic by 16 kcal/mole, while bromine displacement from bromobenzene is calculated to be nearly thermonuetral ($\Delta H = 1.3$ kcal/mole).

Results obtained from this kinetic model suggest that a gas-phase formation mechanism of PBDD is significant. The results of a modeling exercise also demonstrate the sensitivity of the Shaub and Tsang model to changes in the value of one key kinetic parameter (i.e., "dimerization" of haloginated phenol through halogen displacement). Clearly, more research is needed on the gas-phase chemistry and kinetics of brominated and chlorinated organic compounds. Elementary reaction kinetic studies of the key reaction of diphenyl ether formation via halogen displacement by phenoxy are indicated.

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Table 1. Changes to Shaub and Tsang Dioxin Formation Mechanism

$P + P\bullet \longrightarrow PD + Cl$	$10^{9}\exp(-26000/RT)$
$P + P\bullet \longrightarrow PD + Br$	$10^{9}\exp(-11000/RT)$
$PD \longrightarrow D + HCl$	$10^{14}\exp(-45000/RT)$
$PD \longrightarrow D + HBr$	$10^{14}\exp(-41000/RT)$

Table 2. PBDD/PCDD Yields (µg/M^3)

	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
PBDD	4.4E-02	7.8E-02	6.1E-02	3.5E-02	2.0E-02	1.0E-02
PCDD	2.4E-06	1.9E-05	4.4E-05	6.1E-05	7.1E-05	6.6E-05

$P_0 = 300$ µg/M^3
$t = 1.0$ s