

THEORETICAL CALCULATIONS OF THERMODYNAMIC PROPERTIES OF
BROMINATED FLAME RETARDANTS

Grabda M^{1,2}, Oleszek-Kudlak S^{2,3}, Shibata E¹, Nakamura T¹

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1,1 Katahira, 2-Chome, Aobaku, Sendai 980-8577, Japan; ²Institute of Environmental Engineering of Polish Academy of Sciences, M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland; ³Baoshan Iron & Steel Co., Ltd, Environment & Resources Institute, R&D Center, Fujin Road No.655, Baoshan District, Shanghai 201900, China

Introduction

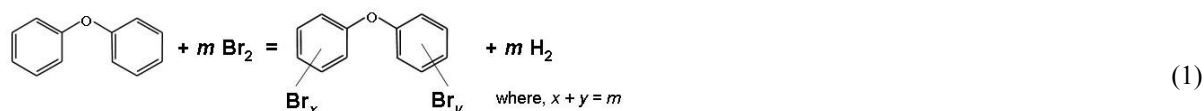
Brominated flame retardants (*BFRs*) attract worldwide scientific attention because of their increasing environmental concentrations combined with the toxicity of the compounds themselves as well as their degradation products. Nevertheless, knowledge of the thermodynamic properties of *BFRs* is scant, limited by pure chemicals availability and analytical complexity.

Although, the most commonly used *BFRs* represent just a few compounds, both the by-products of the industrial synthesis of *BFRs* and their natural biodegradation increase the number of congeners dispersed into the environment¹. The purpose of this study was to obtain a homogenous database of the thermodynamic properties of hexabromocyclododecane (*HBCD*), tetrabromobisphenyl A (*TBBPA*), and all of the congeners of polybrominated phenols (*PBPBs*), diphenyl ethers (*PBDEs*) and biphenyls (*PBBs*).

Materials and Methods

Theoretical calculations of standard state entropy (S°), heat capacity (C_p), enthalpy (ΔH_f°) and Gibbs free energy of formation (ΔG_f°) of selected *BFRs* in the gaseous phase were performed by Density Functional Theory (DFT) methods with Gaussian 03³ at the B3LYP/6-31G(d) level. The zero-point vibrational energies, calculated on optimized molecular structures, were scaled by 0.9804 so that known systematic errors in calculated frequencies might be eliminated.

The S° , C_p , as well as the absolute enthalpy (H°) and the Gibbs free energy (G°) were obtained directly from DFT calculations. The ΔH_f° and ΔG_f° were calculated using designed isodesmic bromination reaction (Eq.1), in combination with thermodynamic relationships derived from the law of energy conservation (Eqs. 2-5). The details of the calculation method used in this study are identical to those in "method 2" described by Li et al.⁴



$$\Delta H_f^\circ = (H^\circ_{\text{PBDE}} + m H^\circ_{\text{H}_2}) - (H^\circ_{\text{DE}} + m H^\circ_{\text{Br}_2}) \quad (2)$$

$$\Delta H_f^\circ_{\text{PBDE}} = \Delta H_f^\circ - m \Delta H_f^\circ_{\text{H}_2} + \Delta H_f^\circ_{\text{DE}} + m \Delta H_f^\circ_{\text{Br}_2} \quad (3)$$

$$\Delta G_f^\circ = (G^\circ_{\text{PBDE}} + m G^\circ_{\text{H}_2}) - (G^\circ_{\text{DE}} + m G^\circ_{\text{Br}_2}) \quad (4)$$

$$\Delta G_f^\circ_{\text{PBDE}} = \Delta G_f^\circ - m \Delta G_f^\circ_{\text{H}_2} + \Delta G_f^\circ_{\text{DE}} + m \Delta G_f^\circ_{\text{Br}_2} \quad (5)$$

Results and Discussion

The quality of the DFT predictions was assessed by a comparison of the calculated results with the few available measurements for brominated arenes. The average standard deviations obtained from these comparisons amount to 2.6, 12.7, and 7.5 kJ·mol⁻¹ for Cp, S° and ΔH_f° , respectively. The high quality of this method has been reported by other authors^{4,6,7}.

The results show that all of the thermodynamic properties are greatly dependent on the number and position of the bromine substituents. A regression analysis performed on the calculated values indicates the increasing stability of all of the congeners with decreasing Br number. Taking into account their differences in the Gibbs free energy of formation, we determined the most and least stable isomers of the *PBPs*, *PBDEs* and *PBBs* in each isomer group (Table 1).

The effects of the bromine substitution positions were studied by the least squares method of statistical analysis. Comparing the calculated regression coefficients corresponding to the number of Br substituents at given locations (Table 2), we found that bromine atoms located at the *ortho* position decreased stability of all congeners much more than those at the *meta* and *para* positions. Hence, congeners with adjacent bromine substituents are always characterized by the highest ΔG_f° , especially if the Br simultaneously adjacent to hydroxyl, ether or phenyl bonds (see Table 1). Some exceptions can be explained by the distinction between intra- and inter-rings interactions.

For *PBDEs*, the repulsive forces related to bromine substitution at two *ortho* positions located on separate rings (2,2'-diBDE) seem to have a stronger effect than those related to two adjacent bromine atoms (2,3-diBDE). This conclusion accorded with the stability of the former isomer being the lowest among its homologues (Table 1), and finds confirmation in the correlation equation (Table 2), in which the effect on the ΔG_f° is lower by 0.524 kJ·mol⁻¹ in the latter case.

Exactly the reverse relation was found for *PBBs* (Table 2), for which the effect of two adjacent bromines (X_{ortho}) is to increase the ΔG_f° by 2.148 kJ·mol⁻¹ above that resulting from substitution at the 2, 2', 6, 6' positions. Hence, the 2,3-diBB was found to be the least stable isomer (Table 2). Comparisons of optimized structures reveal that the closest inter-rings distance between the bromine atoms at the 2, 2', 6, 6' positions is, on average, smaller by 0.25 Å in the case of the *PBDEs* than in the *PBBs* (because of a dihedral bend between the phenyl rings). This reduction leads to stronger repulsive interactions between the bromines substituents, and explains why the congeners with Br at the synchronous 2-2'(6') and/or 6-6'(2') positions are more prevalent among the most unstable *PBDEs*, than those of *PBBs* (Table 1).

The analysis of the *PBPs* isomers challenges the theoretical assumption made by Shaub⁵ that the competitive effect of two synchronous *ortho* interactions to an OH group (2, 6 positions) increases the enthalpy of formation of such molecules. From the correlation equations (Table 2), we can conclude that when a hydroxyl group is symmetrically surrounded by two bromine atoms, some hydrogen bonding may take place between the OH group and the adjacent bromines decreasing the heat and the Gibbs free energy. In fact, all of the most stable congeners of the *PBPs* include bromines at the synchronous 2, 6 position (Table 1).

The results obtained here are likely to be useful in theoretical considerations of the decomposition and transformation pathways of *BFRs*. The order of decreasing stability of the *PBDEs* calculated in this study is in good agreement with the increasing rate of their photochemical degradation reported by Erikson². Such an observation was also reported by Zeng et al.⁷ Just 4 hexa-*BDEs* isomers (in 15 cases analyzed) show a disagreement, but the measured and calculated differences between them are exceptionally small. The formation of the lower brominated *PBDFs* instead of *PBDEs*, reported in the same studies, seems to be thermodynamically favored, and results from the higher stability of the latter compounds in this range (Figure 1). However, a lack of detailed information on the type of *PBDFs* isomers formed excludes the opportunity to consider the transformation mechanism.

Table 1. The most and least stable isomers in different homologue isomers groups

Isomers				Isomers			
<i>BFRs</i>		Most stable	Least stable	<i>BFRs.</i>		Most stable	Least stable
<i>PBPs</i>	mono-	3-	2-	<i>cont.</i>	tri-	2,3,6-; 2,4,6-	2,3,4-
	di-	2,6-	2,3-		tetra-	2,3,5,6-	2,3,4,5-
<i>PBDEs</i>	mono-	3-	2-	<i>PBBs</i>	mono-	3-	2-
	di-	4,4'-	2,2'-		di-	4,4'-	2,3-
	tri-	3,3',5-	2,3,4-		tri-	3,4',5-	2,3,4-
	tetra-	3,3',5,5'-	2,3,4,5-		tetra-	3,3',5,5'-	2,3,4,5-
	penta-	2,3',4,5',6-	2,3,4,5,6-		penta-	3,3',4,5,5'-	2,3,4,5,6-
	hexa-	2,3',4,4',5',6-	2,2',3,4,5,6-		hexa-	2,2',4,4',6,6'-	2,3,3',4,5,6-
	hepta-	2,3,3',4',5,5',6-	2,2',3,4,5,6,6'-		hepta-	2,2',3,3',5,5',6-	2,2',3,3',4,5,6-
	octa-	2,3,3',4,4',5,5',6-	2,2',3,3',4,5,6,6'-		octa-	2,2',3,3',4,4',6,6'-	2,2',3,4,5,6,6'-
	nona-	2,2',3,3',4,4',5,5',6-	2,2',3,3',4,4',5,6,6'-		nona-	2,2',3,3',4,4',5,6,6'-	2,2',3,3',4,4',5,5',6-

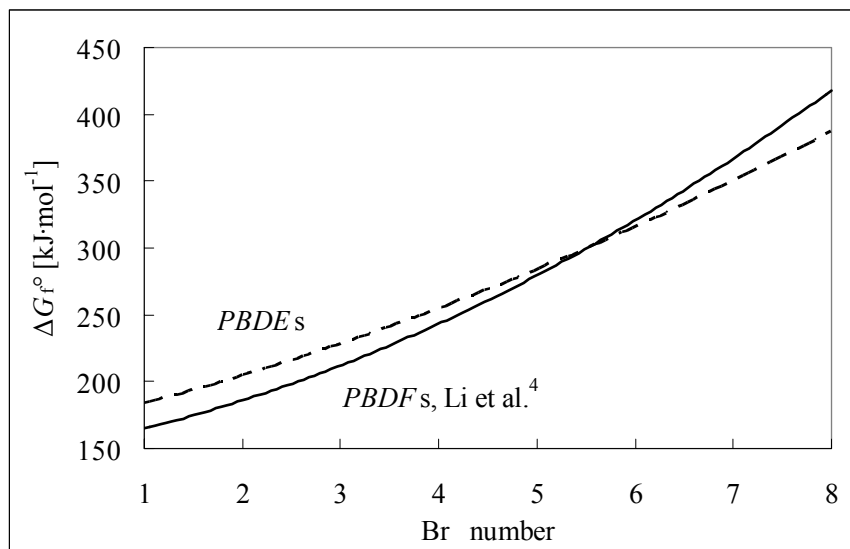
Figure 1. Comparison of stability of *PBDEs* and *PBDFs* congeners (trend lines of polynomial fitting)

Table 2. Effect of number and position of bromine substitutes on thermodynamic properties of *BFRs*. Table includes coefficients of the "least squares" regression equation: parameter = constant + $X_{Br} \cdot N_{Br}$ + $X_{2,6} \cdot N_{2,6}$ + ... + $X_{para} \cdot N_{para}$. All values rounded to three decimal places.

<i>BFRs</i>	Parameter [unit]	Constant	X_{Br}	$X_{2,6}$	$X_{2(2',6,6')}$	$X_{3(3',5,5')}$	$X_{4(4')}$	X_{ortho}	X_{meta}	X_{para}	r^2	SD
<i>PBPs</i>	C_p [J·mol ⁻¹ ·K ⁻¹]	101.833	0	-0.879	16.590	17.294	17.096	-0.157	0.101	-0.105	1.000	0.096
	S° [J·mol ⁻¹ ·K ⁻¹]	313.901	0	-1.907	40.059	41.310	41.422	-2.044	-0.442	0.128	1.000	0.425
	ΔH_f° [kJ·mol ⁻¹]	-98.003	0	-17.007	31.624	24.847	26.028	8.327	3.323	0.516	1.000	0.728
	ΔG_f° [kJ·mol ⁻¹]	-34.651	0	-16.439	22.932	15.783	16.930	8.938	3.455	0.478	0.999	0.818
<i>PBDEs</i>	C_p [J·mol ⁻¹ ·K ⁻¹]	179.503	17.455	-	-0.477	-0.024	-0.281	-0.226	0.136	-0.108	0.996	0.203
	S° [J·mol ⁻¹ ·K ⁻¹]	434.137	38.917	-	-4.770	1.808	2.188	-2.411	0.483	0.086	0.988	3.761
	ΔH_f° [kJ·mol ⁻¹]	40.871	24.308	-	8.618	1.710	2.094	8.797	2.131	1.293	0.997	2.996
	ΔG_f° [kJ·mol ⁻¹]	159.764	15.957	-	10.040	1.171	1.441	9.516	1.986	1.267	0.994	3.584
<i>PBBs</i>	C_p [J·mol ⁻¹ ·K ⁻¹]	163.987	17.433	-	-0.076	-0.322	-0.036	0.056	-0.145	0.010	1.000	1.913
	S° [J·mol ⁻¹ ·K ⁻¹]	398.357	38.608	-	1.009	0.519	1.016	-0.965	0.619	1.653	0.996	7.599
	ΔH_f° [kJ·mol ⁻¹]	186.343	20.132	-	7.726	4.218	3.851	9.311	2.714	2.332	0.998	3.204
	ΔG_f° [kJ·mol ⁻¹]	282.911	11.898	-	7.440	4.058	3.538	9.588	2.515	1.842	0.995	3.674
symbols	N – number of bromine substituents X_{Br} – coefficient corresponding to number of bromine substituents $X_{2(2',6,6')}$, $X_{3(3',5,5')}$, $X_{4(4')}$ – coefficients corresponding to number of bromine atoms at 2 (2', 6, 6'), 3 (3', 5, 5'), 4 (4') positions, respectively (suitable for <i>PBPs</i> - at 2 (6), 3 (5), 4, respectively) X_{ortho} , X_{meta} , X_{para} – coefficients corresponding to number of <i>ortho</i> , <i>meta</i> , <i>para</i> interactions between bromine atoms $X_{2,6}$ – coefficient corresponding to number of Br substituents at position 2 and 6 synchronously (used for <i>PBPs</i> only) r^2 – coefficient of determination SD – standard deviation											

References

1. Cynthia A de Wit. *Chemosphere* 2002; 46:583.
2. Eriksson J, Green N, Marsch G, Bergman Å. *Envir.Sci. Technol.* 2004; 38:3119.
3. Frish E, Frish MJ, Trucks GW. *Gaussian 03 User's Reference, Manual version 7.0*, 2004:330 Gaussian Inc., Carnegie, ISBN 0-9727187-0-2.
4. Li X-W, Shibata E, Nakamura T. *Materials Transactions* 2003; 44:1004.
5. Shaub W M. *Thermochimica Acta* 1983; 62:315.
6. Zeng X., Freeman PK, Vasil'ev YV, Voinov VG, Simonich SL, Barofsky DF. *J. Chem. Eng. Data* 2005; 50:1548.
7. Zhai Z, Wang Z. *Journal of Molecular Structure: THEOCHEM* 2005; 724:221.