

Theoretical calculation of thermodynamic properties of Polybrominated Diphenyl Ethers and prediction of photodecomposition products of BDE-209

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Introduction

Polybrominated Diphenyl Ether (PBDE) flame retardants are widely used as additives in polymers for textiles, electronics, and home furnishings. They have been widely detected in biotic and abiotic matrices including sediments, air, water, fish, marine mammals, human plasma, and human milk. As the use of PBDEs has increased in recent years, their concentrations in the environment have also increased. Although extensive studies have been conducted to measure the presence of PBDEs in the environment, their vapor pressures, and their octanol-air partition coefficients, none have been conducted to measure their thermodynamic properties. This is due to the limited availability of pure compounds and to experimental difficulties due to photodegradation. Therefore, theoretical calculations are of interest for estimating the thermodynamic properties of PBDEs.

To better understand and describe the environmental fate of PBDEs, photochemical degradation reactions have been studied. The photochemical degradation of 15 PBDEs was studied in methanol/water by UV light.¹ The photochemical reaction rates were found to decrease with the decreasing number of bromine substituents in the molecule but were also, in some cases, influenced by the PBDE substitution pattern. Studies were performed^{2,3,4} on the photolysis of BDE-209 dissolved in various solvents and matrices in both sunlight and/or artificial UV light and the stepwise debromination to form lower brominated diphenyl ethers was observed. In the most recent study⁴, the potential intermediates in reductive debromination of BDE-209 to BDE-47 was described. However, the mechanism of the stepwise photodegradation of BDE-209, as well as the dependence of photochemical degradation rate on solvent, was not discussed in these studies. Theoretical calculations should be carried out to better understand the mechanism of PBDE photodecomposition and predict the relative abundance of photodecomposition products.

Materials and Methods

Density Functional Theory (DFT) calculations were carried out⁵ to estimate the enthalpy of formation, ΔH_f , and the Gibbs free energy of formation, ΔG_f , of PBDEs in the gas phase at 298.15 K and 101.325 kPa. Similar calculations have been performed on PBDDs,⁶ PCDDs⁷ and PCDFs.⁸ 39 PBDE congeners were selected according to the commercial availability of standards and importance in environmental research to perform calculation of their thermodynamic properties. Using Gaussian 03, geometry optimizations and energy calculations were performed at the B3LYP/6-31G(d) level. The absolute enthalpy (H), as well as the absolute Gibbs free energy (G), were obtained from the Gaussian output file in Hartrees and converted to kJ/mol. Time-dependent density-functional theory (TD-DFT) was used to calculate excitation energies of PBDEs.

In previous studies, isodesmic reactions were applied to estimate the thermodynamic properties of PBDDs,⁶ PCDDs,⁷ and PCDFs.⁸ Given the accuracy of these theoretical calculations for PBDDs and PCDDs, it seems reasonable to expect that estimates of the thermodynamic properties of PBDEs, from DFT calculations based on isodesmic reactions, will be similarly accurate. In this study, reaction: $DE + n \text{ bromobenzene} = PBDE + n \text{ benzene}$ served as the basis for calculating ΔH_f and ΔG_f for the PBDEs. DFT calculations obtain absolute enthalpies of the products and reactants. The ΔH_f for any given PBDE can be calculated knowing the literature values of ΔH_f for benzene, DE and bromobenzene. The same method was used to calculate ΔG_f .

Results and Discussion

Because of the low energy barrier for the phenyl rings' rotation about the ether bond, most congeners have more than

one stable conformations. Through DFT calculations it was found that these stable conformations are connected by appropriate transition states. In general, the energy differences between the conformations of a PBDE congener, as well as energy barrier for the transformation between conformations, were found to be much smaller than the energy differences between congeners within homologues. The less stable conformations of a congener can not simply be disregarded in favor of the most stable conformations when characterizing a congener. The energies of the various conformations should be weighted in accordance with their relative abundances when computing the average energy of the congener. The equilibrium constant, k , for conversion from one conformation to another can be calculated from the difference in ΔG_f between the conformations: $\Delta(\Delta G_f) = -RT \ln(k)$

It was determined in an earlier study⁶ that the energy differences between PBDD congeners are strongly affected by the intramolecular halogenic repulsion, position, and number. An analysis of these factors in the present study indicates that the inter-congener energy differences for PBDEs are similarly affected. Previous experiments⁹ showed that PBDE congeners with one fully brominated phenyl ring, such as 2,3,4,5,6-PeBDE, 2,3,4,4',5,6-HxBDE, 2,2',3,4,4',5,6-HpBDE, and 2,3,3',4,4',5,6-HpBDE, are the most susceptible to photochemical decomposition among the highly brominated PBDEs. The results calculated in our study indicate that these congeners are the least stable among the respective homologues, which is consistent with experimental observation.⁹

Based on the thermodynamic values calculated in this study, PBDE congeners become less stable as the number of bromines increases (Figure 1). Deca-BDE, which has a fully brominated structure, has the highest ΔG_f . Indeed, deca-BDE has been observed in previous studies^{1,3,10} to be photolytically unstable. The other 38 PBDE congeners studied here have an entropy increase during formation. The order of stability calculated in this study (Figure 1) is in agreement with the increasing rate of PBDE decomposition with increasing numbers of bromine reported in an early study.¹

Lee et al.,⁷ based on Benson's group additivity method (GAM),¹¹ analyzed the effect of chlorination position and Cl intramolecular repulsion on the energy of formation for PCDDs. This method has been adapted in this study to quantitatively analyze the effect of Br substitution

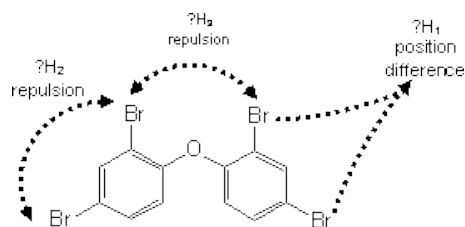


Figure 2. Group additivity components for 2,2',4,4'-TetraBDE

patterns on the energy of formation for PBDEs. All of the components of this method are illustrated schematically in Figure 2 for a PBDE congener. ΔH_1 is the difference in enthalpy compared to meta position on the phenyl ring; ΔH_2 is intramolecular Br-Br repulsion in one phenyl ring; and ΔH_3 is intramolecular Br-Br repulsion between two phenyl rings. Intramolecular repulsion causes the ΔH_f to increase nonlinearly with increasing number of bromines. This is reflected in the positive non-linear curvature of a plot of DFT calculated ΔH_f vs. bromine number (Figure 1). Furthermore, the congeners with the same number of bromines also differ due to various substitution positions and different repulsion effects. This is also demonstrated in Figure 1 by the scattered points for the DFT calculated values.

It is of interest to look at the trend of ΔH_f without considering the Br substitution position and intramolecular Br-Br repulsion. GAM corrected ΔH_f is the result of ΔH_f from DFT calculation subtracted by the sum of ΔH_1 , ΔH_2 and ΔH_3 . In contrast to the curve of ΔH_f from DFT calculation, the values of GAM corrected ΔH_f fall very well on a straight line when plotted against the number of bromines (Figure 1). The slope of the line resulting from linear regression implies that the ΔH_f increases 21.98 kJ/mol for each addition of a single bromine when the substitution position and intramolecular repulsion are not considered. The GAM model can be used to predict the thermodynamic properties of all of the 209 PBDE congeners.

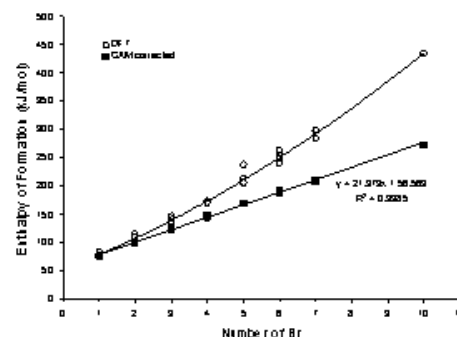


Figure 1. Comparison of ΔH_f between DFT calculation and GAM corrected results.

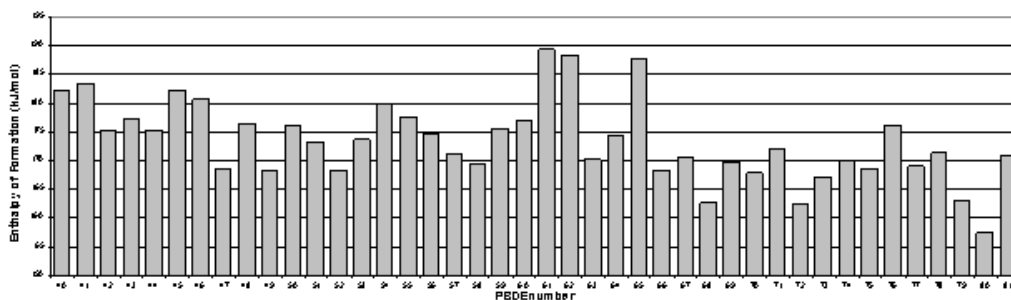


Figure 3. ΔH_f for all of the Tetra-BDEs from GAM model

The enthalpies of formation of the Tetra-BDEs were calculated using the GAM model and shown in Figure 3. The result shows that, among the Tetra-BDEs, BDE-68, BDE-72, BDE-79, and BDE-80 are the most stable congeners. Previous studies^{3,4} on photodegradation of BDE-209 found that BDE-47 and 49 were the most abundant Tetra-BDEs of all products, however, the most stable Tetra-BDE congeners, i.e. BDE-68, BDE-72, BDE-79, and BDE-80, were not studied or measured in the experiments. BDE-209 accounts for over 80% of the total annual global production of PBDEs and it is not banned currently in the US. Study on the photodecomposition of BDE-209 may clarify the relationship between the congener profiles in the environment and the profiles of commercial PBDE products. The potential intermediates in reductive debromination of BDE-209 were analyzed in the early study.⁴ But the mechanism needs to be discussed to predict the complete photo degradation pattern of BDE-209.

A previous study¹ determined the absorption spectra of several PBDE congeners. TD-DFT calculation in this study shows that the absorption bands of each congener match the excitation from ground state to singlet excited state. The relaxed potential energy scan of BDE-99 dissociation for the ground state and the first excited singlet state are shown in Figure 4. From Figure 4 it is clear that there is no transition state in the process of the dissociation of the PBDEs. DFT calculations were also applied to calculate the dissociation energies of PBDE congeners which are the difference between a PBDE congener and its dissociation products: a lower brominated diphenyl ether radical and Br radical. The calculated dissociation energies match the energy gap between the equivalent point and the point when the C-Br bond length is infinite.

In this study, the GAM model was also used to predict the dissociation energy of a specific bromine atom for PBDEs. The sum of the repulsion and positional effects of a specific bromine atom for several PBDEs were calculated and found to be linearly correlated to the dissociation energies calculated by the DFT method. According to the magnitude of the dissociation energies, the most favored photodecomposition products and their relative abundance were predicted. The results suggest that the photodecomposition of BDE-209 follows certain pathways determined by the dissociation energies leading to BDE-47 and BDE-49. Our results suggest that the photodecomposition of PBDEs is kinetically, not thermodynamically controlled.

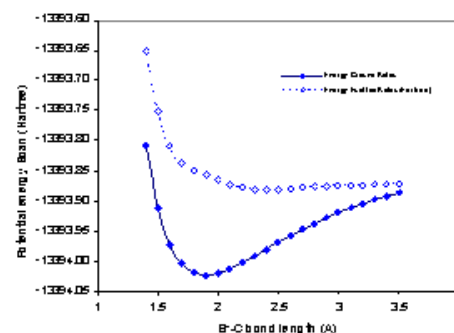


Figure 4. Relaxed potential energy scan of BDE-99 dissociation to BDE-49

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References

1. Eriksson, J.; Green, N.; Marsh, G.; Bergman, (2004) *Environmental Science and Technology*, 38, 3119.

2. Watanabe, I.; Tatsukawa, R. (1987) *Bulletin of environmental contamination and toxicology* FIELD Publication Date:1987 Dec, 39, 953.
3. Soderstrom, G.; Sellstrom, U.; de Wit Cynthia, A.; Tysklind, M. (2004) *Environmental science & technology* FIELD Publication Date:2004 Jan 1, 38, 127.
4. Bezares-Cruz, J.; Jafvert, C. T.; Hua, I. (2004)*Environmental Science and Technology*, 38, 4149.
5. Zeng, X.; Freeman, P. K.; Vasil'ev, Y. V.; Voinov, V. G.; Simonich, S. L.; Barofsky, D. F. (2005)*Journal of Chemical and Engineering Data* (submitted).
6. Li, X.-W.; Shibata, E.; Nakamura, T. (2003) *Journal of Chemical and Engineering Data*, 48, 727.
7. Lee, J. E.; Choi, W.; Mhin, B. J. (2003) *Journal of Physical Chemistry A*, 107, 2693.
8. Zhu, L.; Bozzelli, J. W. (2003) *Journal of Physical and Chemical Reference Data*, 32, 1713.
9. Peterman, P. H.; Orazio, C. E.; Feltz, K. P. (2003) *Organohalogen Compounds*, 63, 357.
10. Herrmann, T.; Schilling, B.; Paepke, O. (2003) *Organohalogen Compounds*, 63, 361.
11. Benson, S. W. (1976) *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*. 2nd Ed.