

ESTABLISHMENT OF FREE ENERGIES OF THE FORMATION OF POLYBROMINATED DIBENZO-*p*-DIOXINS AND FURANS

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Introduction

There is much less information on polybrominated dibenzo-*p*-dioxins and furans (PBDDs/PBDFs) than on their chlorinated analogues (PCDDs/PCDFs), and there are very few experimental data on their physical and chemical properties. The analytical methods for separating and identifying the individual brominated congeners are much less advanced than those for their chlorinated analogues, and only few reference standards are available. Current analytical methods are able to quantify total brominated homologue groups and also to detect but not quantify the mixed brominated/chlorinated congeners (PXDDs/PXDFs). Because of the complexity of analytical procedures and lack of reference standards, it has been possible to characterize and determine only a small number of PBDDs/PBDFs and PXDDs/PXDFs.

The practical purpose of the study is to obtain a consistent set of thermodynamic values for PBDDs/PBDFs and PXDDs/PXDFs and to consider the formation behaviors of PBDDs/PBDFs and PXDDs/PXDFs in the flue gas of the incinerator using the set of thermodynamic values. In this study, the thermodynamic properties (heat capacity, entropy, enthalpy and Gibbs energy of formation) in the gaseous state were computed for all PBDDs/PBDFs using density functional theory (DFT)¹, and a simple deduction for the formation of them was concluded using the standard free energies of formation.

Methods

Ab initio molecular orbital calculations were carried out with the Gaussian 98 programs.¹ Becke's three-parameter hybrid functional combined with the gradient-correlation functional of Lee, Yang and Parr (LYP), denoted B3LYP, was employed in the computations using DFT. The all-electron 6-31G(d) basis set was employed. Geometries were optimized using analytic gradient techniques, i.e. the Berny algorithm with redundant internal coordinates. The stationary points on the potential energy surface were characterized by calculations of vibrational frequencies, which were done analytically at DFT levels. Following the geometry optimization (Opt), frequencies (Freq) were calculated using the same method at a stationary point. The zero-point vibrational energies (ZPE) calculated at the DFT level were scaled by 0.9804.

Throughout this paper, all calculations for PBDDs/PBDFs were carried out with B3LYP/6-31G(d) Opt Freq. At present this computational level is the highest one which has been applied to calculate the thermodynamic values of dioxin congeners serially.^{2,3}

The equations used for computing thermochemical data in Gaussian programs are derived from statistical thermodynamics. Two key ideas of statistical thermodynamics are the Boltzmann distribution and the partition function. The partition function is like a thermodynamic wavefunction, in the sense that it contains all thermodynamic information about the system, just as the quantum mechanical wavefunction contains all dynamic information.

The entropy (S) and heat capacity of constant pressure (C_p) can be evaluated from the following relations.

$$S = S_{trans} + S_{rot} + S_{vib} \quad (1)$$

$$C_p = C_{trans} + C_{rot} + C_{vib} \quad (2)$$

where subscripts of trans, rot and vib indicate translational, rotational and vibrational entropy and heat capacity, respectively, which can be calculated by the statistical thermodynamic equations using the vibrational frequency.⁴

The absolute enthalpy (H) and Gibbs energy (G) values of the molecule can be obtained through DFT calculation, it is easy to obtain the reaction enthalpy and Gibbs energy for any reaction using these energy values by eq. 3 and 5. In another way, the reaction enthalpy and Gibbs energy can be calculated by eq. 4 and 6, respectively.

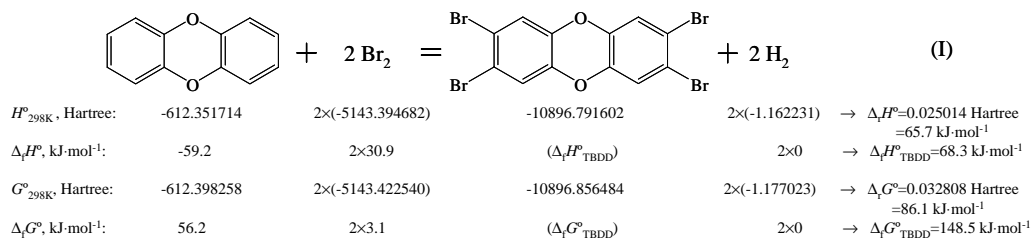
$$\Delta_r H^\circ(298\text{K}) = \sum (H_{298\text{K}})_{\text{products}} - \sum (H_{298\text{K}})_{\text{reactants}} \quad (3)$$

$$\Delta_r H^\circ(298\text{K}) = \sum (\Delta_f H_{298\text{K}}^\circ)_{\text{products}} - \sum (\Delta_f H_{298\text{K}}^\circ)_{\text{reactants}} \quad (4)$$

$$\Delta_r G^\circ(298\text{K}) = \sum (G_{298\text{K}})_{\text{products}} - \sum (G_{298\text{K}})_{\text{reactants}} \quad (5)$$

$$\Delta_r G^\circ(298\text{K}) = \sum (\Delta_f G_{298\text{K}}^\circ)_{\text{products}} - \sum (\Delta_f G_{298\text{K}}^\circ)_{\text{reactants}} \quad (6)$$

where $\Delta_r H^\circ$ and $\Delta_r G^\circ$ are the reaction enthalpy and Gibbs energy, $\Delta_f H^\circ$ and $\Delta_f G^\circ$ are the standard-state enthalpy and Gibbs energy of formation of the ideal gas, respectively. Combining these equations and using the experimental data of enthalpy and Gibbs energy of formation for H_2 , Br_2 , and dibenzo-*p*-dioxin (DD), the unknown enthalpy and Gibbs energy of formation values of 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD) can be calculated from the reaction (I) (all reactants and products are in gas state).



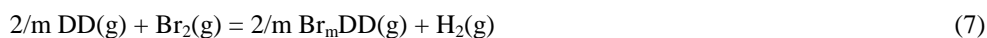
The of enthalpy and Gibbs energy of formation values of TBDD calculated from reaction (I) are 68.3 kJ·mol⁻¹ and 148.5 kJ·mol⁻¹, respectively.

Results and Discussion

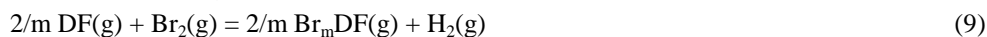
To assess the accuracy of the methods used to predict the enthalpy and Gibbs energy of formation, the thermodynamic properties of 16 compounds (Brominated arenes) were first calculated, and compared with available experimental data. The calculated results of entropy of formation have been compared with experimental data in our reports^{5,6} and they showed a good agreement. On the properties of heat capacity and absolute entropy, the calculation results obtained by B3LYP/6-31G(d) seem to be accurate, since Gaussian employs the mature theoretical methods of statistics thermodynamics to compute these two thermodynamic properties, and this computational level is moderate.

The calculation results of S , C_p , $\Delta_f H$ and $\Delta_f G$ for 76 PBDDs and 136 PBDFs in the gas phase at 298.15 K (for C_p , the temperature range is from 298.15 to 1500 K) and 101.325 kPa have been already reported in a table style.^{5,6} Among 10 isomers of dibromodibenzo-*p*-dioxins, the standard Gibbs energies of formation for 2,7-DiBDD and 2,8-DiBDD are lower than those of the other 8 isomers of dibromodibenzo-*p*-dioxins. It means that these 2 isomers are more stable, and easier to form during formation process. 1,3,7-TrBDD, 1,3,8-TrBDD and 2,3,7-TrBDD are easier to form than the other 11 isomers of tribromodibenzo-*p*-dioxins. In the same way, for the isomers of tetrabromodibenzo-*p*-dioxins, 1,3,6,8-TeBDD, 1,3,7,8-TeBDD, 1,3,7,9-TeBDD, and 2,3,7,8-TeBDD (the most toxic compound in PBDDs) are easier to form than the other 18 isomers. For the isomers of pentabromodibenzo-*p*-dioxins, 1,2,4,6,8-PeBDD, 1,2,4,7,8-PeBDD and 1,2,4,7,9-PeBDD are easier to form than the others. For the isomers of hexabromodibenzo-*p*-dioxins, 1,2,4,6,7,9-HxBDD and 1,2,4,6,8,9-HxBDD are easier to form than the others. Comparing with PBDDs, the enthalpies and Gibbs energies of formation for PBDF isomers are more variable. The enthalpies and Gibbs energies of formation for isomers which have bromine substitutions in 1 and 9 positions are much higher than those of the others. The reason is that the bromine atoms in 1 and 9 positions are close. The distance between the two bromine atoms in 1 and 9 positions is about 3.3×10^{-10} m, it is in the same level with the distance between adjacent bromine atoms (ortho) in the same benzene ring. The Gibbs energies of 1,7-DiBDF, 1,3,7-TrBDF, 1,3,6,8-TeBDF, 1,3,4,6,8-PeBDF and 1,3,4,6,7,8-HxBDF are the lowest among their isomers, respectively. 2,3,7,8-TeBDF has a low Gibbs energy of formation similar to 1,3,6,8-TeBDFs and it is also stable among TeBDFs.

The formations of PBDDs/PBDFs are also considered thermodynamically using the reaction free energies for PBDDs/PBDFs as following equation;



$$\Delta_r G_7^\circ = 2/m \Delta_f G_{\text{Br}_m \text{ DD}}^\circ + \Delta_f G_{\text{H}_2}^\circ - 2/m \Delta_f G_{\text{DD}}^\circ - \Delta_f G_{\text{Br}_2}^\circ \quad (8)$$



$$\Delta_r G_9^\circ = 2/m \Delta_f G_{\text{Br}_m \text{ DF}}^\circ + \Delta_f G_{\text{H}_2}^\circ - 2/m \Delta_f G_{\text{DF}}^\circ - \Delta_f G_{\text{Br}_2}^\circ \quad (10)$$

where m indicates a number of bromine atoms in each molecule. Figure 1 and 2 show the change of reaction free energy for each stable isomer of PBDDs and PBDFs, respectively. As the substitute number of bromine increases, the reaction free energies of gaseous PBDDs and PBDFs increase. From Figs1 and 2, it can be suggested thermodynamically that the formations of PBDDs/PBDFs cannot occur so easily compared with PCDDs/PCDFs because the reaction free energies of eq.8 and 10 are positive.

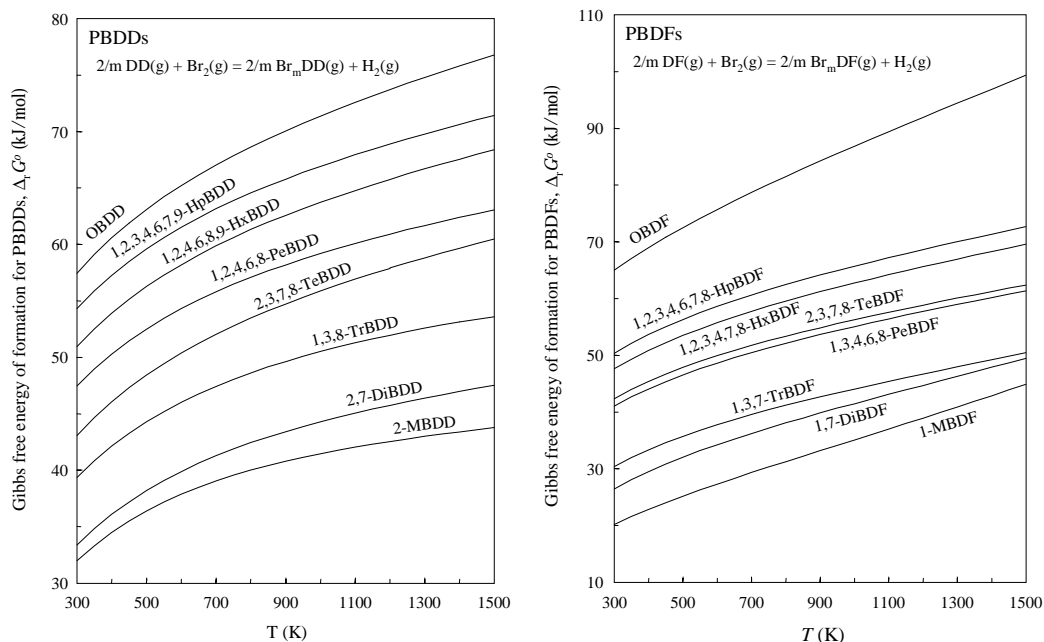


Fig.1 Gibbs energies of formation for PBDDs. **Fig.2** Gibbs energies of formation for PBDFs.

Acknowledgements

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