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DFT calculation on 204 polychlorinated biphenyls: their thermodynamic function and implication of Cl substitute position

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Abstract

The thermodynamic function, including total energy (TE), enthalpy (H^0), entropy (S^0) and free energy (G^0) for 204 polychlorinated biphenyls (PCBs), were predicted by fully optimized calculation at the B3LYP/6-31G* level. With design of isodemic reactions, the standard formation heat (ΔH_f^0), standard formation free energy (ΔG_f^0) of PCBs were obtained. In addition, the dependences of these thermodynamic parameters on the number and position of chlorine substitute were discussed. It was suggested that TE, H^0 and G^0 of PCBs vary greatly with chlorine substitute at different positions, in which the order of increase of parameter value being position 2(6) ≫ position 3(5) > position 4. It was also found that the data of these thermodynamic parameters all increase in the case of the two chlorine substitutes at the same aromatic ring, compared with that at two aromatic rings, the increase effect being *ortho* ≫ *meta* > *para*. With addition of each chlorine atom in PCB, the increase of S^0 is about 30 J/mol K, and also the relative stability of PCB congeners at 573.15 K was proposed in this work.

Keywords: Dioxin; Polychlorinated biphenyl; Density functional theory; Thermodynamic function

1. Introduction

Polychlorinated biphenyls (PCBs), as one category of dioxins, possess much potential hazard to the environment due to their wide application as raw materials in chemical industry. As known, the thermodynamic data of dioxins are very important for studying the formation mechanism of these compounds and are also useful to explore an effective way to reduce these toxic materials in the environment [1–3]. In addition, knowledge of precise dioxin structures is necessary in investigation of the quantitative structure–activity relationship of dioxin congeners and their interaction mechanisms to organism. However, it is impossible to determine all the thermodynamic properties and structures of dioxin compounds, attributed to many dioxin congeners and the complexity of them. Fortunately the thermodynamic properties of dioxins, such as PCDDs, PCDFs and PCBs, can be predicted by molecular orbital computation with the development of computer science. In the past decade, much work has been done by semi-empirical molecular orbital method, for example, Koester and Unsworth et al. reported the computational result about PCDD by MNDO [1,2]. Wehrmeier et al. [3] studied PCDD and PCDF by AM1 and Saito et al. [4] reported the thermodynamic parameters of PCDF and PCB using PM3. In addition, the structure–activity relationship of PCB was investigated by Xiaodong Wang [5] and Huang Jun [6] by AM1.

Density functional theory (DFT) has much advantage in studying the structure and property of many complex organics [7,8]. To achieve useful thermodynamic data of these substances, it is possible and effective to obtain standard formation heat and free energy of a series of important dioxin compounds by designing isodemic reactions [9]. For instance, Lee et al. reported the PCDD parameter data calculated with B3LYP/6-31G** method [10], which results in higher precision than semi-empirical

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methods such as MNDO, AM1 and PM3. Li Zhu et al. used density functional B3LYP/6-31G** and B3LYP/6-311+G(3df,2p) and calculated the ΔH_f^0, S^0 and $C_p^0(T)$ of 15 dioxin congeners including 2,3-benzodioxin, 2,3-benzofuran, 12 monochloro and dichloro dibenzo-*p*-dioxins and dibenzofurans, etc. [11]. We reported the thermodynamic data and relative stability of 74 TCDD isomers obtained by computation at B3LYP/6-311G**, and our result suggested that the isomers with low free energy have high formation ratio, which is consistent with the observed formation percentage of PCDD isomers from incinerator [12,13].

The present study aims at fully computational optimization of 204 PCBs. With observation of the thermodynamic data of PCBs, the dependences of these parameters on the number and position of chlorine substitute in PCBs were determined. By designing isodemic reactions, the standard formation heat (ΔH_f^0), standard formation free energy (ΔG_f^0) and the formation free energy at 573.15 K ($\Delta G_f^{573.15}$) for all PCBs were obtained. Also, the stability order of isomers for each isomer group at 573.15 K was discussed in accordance with the magnitude of ($\Delta G_f^{573.15}$).

2. Computational method

In this work, the B3LYP/6-31G* method [14–16] in GAUSSIAN98 program [17] was employed for fully optimization of 204 PCBs to get total energy (TE), enthalpy (H^0), entropy (S^0) and free energy (G^0) of these compounds. The (ΔH_f^0) and (ΔG_f^0) of PCBs were obtained by designing isodemic reactions. All these computations, however, were performed on a Pentium IV 2.66G computer.

3. Results and discussion

3.1. Relation of the number and position of chlorine substitute to TE, H^0 and G^0

TE of 204 PCBs was, respectively, listed in Table 1. With careful analysis of the table, the obvious correlation of TE and the position of chlorine substitute in PCB molecule can be found, i.e. TE of 3-monochlorinated biphenyl (3-MCB) is very close to that of 4-MCB, with TE of 2-MCB the highest in the three isomers, which is about 0.0049 hartree (12.86 kJ/mol) higher than that of 3-MCB and 4-MCB. This suggests the MCB molecule with chlorine substitute at position 2 is the most unstable one, due to the relatively larger repelling force between the chlorine at position 2 and the other aromatic ring. While in the 12 isomers of dichlorinated biphenyl (DCB), 4,4′-DCB has the lowest TE and 2,3-DCB has the highest. This is because the two chlorine atoms are at different aromatic ring for the former, while the two *ortho* chlorines are at the same ring for the latter with one chlorine atom at position 2. With observation of other congeners, similar correlation of TE against the number of chlorine substitutes and their position can be discovered.

If the numbers of chlorine atoms at positions 2(6, 2′, 6′), 3(5, 3′, 5′) and 4(4′) are defined as $N_{2(6)}$, $N_{3(5)}$ and N_4, the number of chlorine at *ortho*, *meta* and *para* positions are symbolized as N_o, N_m and N_p, respectively, the correlation of TE and the number of N for PCB can be described as follows using the least square method:

$$\begin{aligned}\mathrm{TE} = {} & -463.30644 - 459.59165N_{2(6)} \\ & - 459.59515N_{3(5)} - 459.59560N_4 \\ & + 0.00508N_o + 0.00128N_m \\ & + 0.00086N_p(\text{hartree})\end{aligned} \tag{1}$$

$$r^2 = 1.0000 \quad \mathrm{SD} = 0.0008$$

where r^2 is the square of correlation coefficient, SD is standard deviation.

It can be seen from Eq. (1), the congener with chlorine at position 2 is the least stable one, and its TE is higher than that with chlorine at position 3 and 4 by 0.00350 hartree (9.19 kJ/mol) and 0.00359 hartree (10.37 kJ/mol), respectively. On the other hand, the TE of PCB congener with chlorine substitutes at *ortho*, *meta* or *para* positions increases by 0.00508 hartree (13.34 kJ/mol), 0.00128 hartree (3.36 kJ/mol) and 0.00086 hartree (2.26 kJ/mol), respectively, than the isomer with chlorines at two benzene rings.

Similarly, the correlation of H^0 and G^0 to the number N can be expressed as Eqs. (2) and (3) in Table 2. In view of Eqs. (2) and (3), it is suggested that the H^0 and G^0 of PCBs vary obviously with chlorine substitute at different positions, in which the order of increase of H^0 and G^0 value being position 2 ≫ position 3 > position 4, while the H^0 and G^0 value of PCBs with chlorines at the same aromatic ring is higher than that with chlorines at two aromatic rings, and the increase order is *ortho* ≫ *meta* > *para*, in which the least stable congener is the one with *ortho* chlorines.

3.2. Relation of the number and position of chlorine substitute to S^0

Relation of the number and position of chlorine substitute to S^0 can been seen in Eq (4) in Table 2. From the equation, the number of chlorine substitute has obvious effect on entropy, but the effect of spatial chlorine position on the parameter S^0 is minor. With addition of each chlorine atom, the increase of S^0 is around 30 J/mol K.

3.3. Calculated ΔH_f^0, ΔG_f^0 and $\Delta G_f^{573.15}$ value for PCBs

Up to date, there has been thermodynamic data reported for PCBs, which were only obtained by PM3 [4], a semi-empirical molecular orbital method. To get more precise