Enthalpies of Formation of Dibenzo-*p*-dioxin and Polychlorinated Dibenzo-*p*-dioxins Calculated by Density Functional Theory

Olga V. Dorofeeva* and Vladimir S. Yungman

Glushko Thermocenter, Associated Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya St. 13/19, Moscow 125412, Russia

Received: September 12, 2002; In Final Form: December 23, 2002

The enthalpies of formation for gaseous dibenzo-*p*-dioxin and 75 polychlorinated dibenzo-*p*-dioxin congeners were calculated at the B3LYP density functional theory level using isodesmic reactions. Calculated values are compared with experimental data for dibenzo-*p*-dioxin, 1-chlorodibenzo-*p*-dioxin, 2-chlorodibenzo-*p*-dioxin, and 2,3-dichlorodibenzo-*p*-dioxin as well as with previous results from group additivity estimations and theoretical calculations. The calculated enthalpy of formation of dibenzo-*p*-dioxin, −52.8 ± 3.0 kJ/mol, is in good agreement with the recent experimental value of −50.1 ± 2.2 kJ/mol, whereas the discrepancies from experimental data for chlorinated dibenzo-*p*-dioxins range from 2 to 20 kJ/mol. The uncertainties of calculated enthalpies of formation are estimated to be from 3 to 30 kJ/mol.

Introduction

Due to their extreme toxicity in the environment, polychlorinated dibenzo-*p*-dioxins (PCDDs) have received much scientific attention in recent years. Knowledge of the thermodynamics of PCDDs is very important in thermodynamic modeling the reaction paths relating to their formation, destruction, and combustion. Because of the large number of PCDD congeners and the high toxicity of some isomers, experimental data on their thermodynamic properties are difficult to obtain. Only for dibenzo-*p*-dioxin (DD), 1-chlorodibenzo-*p*-dioxin (1-CDD), 2-chlorodibenzo-*p*-dioxin (2-CDD), and 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD) were the enthalpies of formation ($\Delta_f H^\circ_{298}$) determined from calorimetric studies.[1−5] As a result, the group contribution methods[6−9] and semiempirical calculations[10,11] were used to estimate the $\Delta_f H^\circ_{298}$ values for PCDDs. Quite recently the enthalpies of formation of the 10 most toxic PCDDs were computed by density functional B3LYP method using different types of isodesmic reactions.[12] There is appreciable discrepancy between the enthalpies of formation estimated in all these studies.

Accurate determination of enthalpies of formation of PCDDs from theoretical calculations is very difficult. The $\Delta_f H^\circ_{298}$ values at sufficient accuracy can be obtained only from very high level calculations, such as G3, CBS-Q, MP6, QCISD(T), and CCSD(T). These models include a significant fraction of the electron correlation energies. However, such calculations are computationally too expensive and untested for large chlorinated molecules. One method that has recently been successfully applied to the estimation of enthalpies of formation is the use of ab initio Hartree−Fock or density functional theory (DFT) calculations combined with isodesmic reactions approach. DFT (though not fully ab initio) method has the advantage over Hartree−Fock calculations for allowing the correlation effects to be partly included in a calculation. The B3LYP method, which is one of the most popular DFT methods, has the mean absolute deviation of 13 kJ/mol for a set of 148 gas-phase $\Delta_f H^\circ_{298}$ values of relatively small molecules.[13] This result is based on the enthalpies of formation obtained by a standard approach using the calculated atomization energies. The agreement between theory and experiment can be improved when the calculation of the enthalpy of formation is based on the isodesmic reaction rather than the atomization reaction.[14,15] An isodesmic reaction is one in which the number of bonds of each type is conserved on the two sides of the reaction, and then one might expect the cancellation of errors arising from insufficient treatment of electron correlation and incompleteness of the basis sets. In recent years the method of isodesmic reactions has been employed to evaluate the $\Delta_f H^\circ_{298}$ values of different molecules.[15−20] The B3LYP level of theory combined with isodesmic reactions is used in this work to estimate the enthalpies of formation of DD and PCDDs.

One of the deficiencies of the isodesmic reaction approach is that the calculated $\Delta_f H^\circ_{298}$ value is dependent on the choice of reaction. An isodesmic reaction leads to more accurate results if (1) there is a similarity of bonding environment in the reactants and products and (2) the experimental enthalpies of formation of reference molecules are determined with high accuracy. In this work, we discuss to what extent the isodesmic reactions designed for PCDDs fulfill these conditions. Special attention is given to the accuracy of the calculated $\Delta_f H^\circ_{298}$ values.

Computational Methods

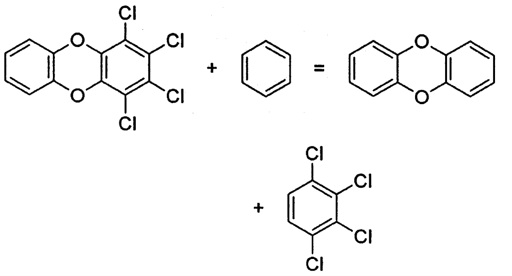
The calculations were carried out at the B3LYP density functional theory level using the Gaussian 98 system of programs.[21] The structural parameters were fully optimized at the B3LYP/6-31G(d,p) level of theory. Vibrational frequencies were calculated at the same level. We have used a factor of 0.96 [22] to scale the B3LYP frequencies in the calculation of zero-point energies and thermal corrections. To see how the large basis set results in an improvement of calculated values, the optimized geometries of DD, 1-CDD, 2-CDD, 2,3-DCDD, 1,2,3,4-TCDD, 2,3,7,8-TCDD, and OCDD were also used to obtain the electronic energies in B3LYP/6-311+G(3df,2p) single point calculations.

---

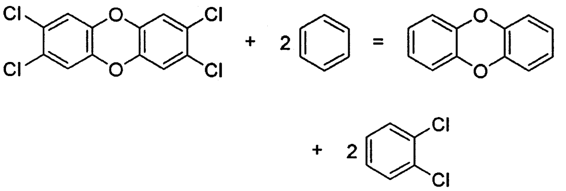
* To whom correspondence should be addressed. E-mail: olga.d@ru.net.

10.1021/jp026973y CCC: $25.00 © 2003 American Chemical Society
Published on Web 04/01/2003

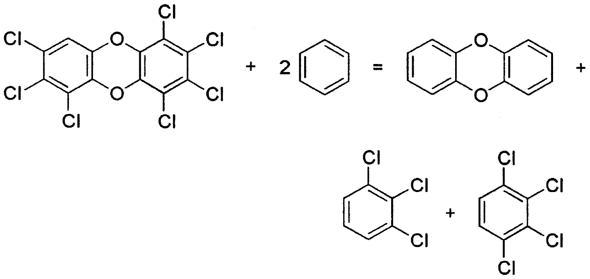
To validate the accuracy of calculations based on isodesmic reaction schemes, it is necessary to select molecules that are similar to PCDDs and for which accurate thermochemical data are available. In this work, we use the following set of nine reference molecules: dibenzo-*p*-dioxin; benzene; chlorobenzene; 1,2-, 1,3-, and 1,4-dichlorobenzenes; 1,2,3- and 1,2,4-trichlorobenzenes; and 1,2,3,4-tetrachlorobenzene. For example, the following isodesmic reactions were used to derive the $\Delta_f H^\circ_{298}$ values of 1,2,3,4-TCDD, 2,3,7,8-TCDD, and 1,2,3,4,6,7,8-HpCDD:



(1)



(2)



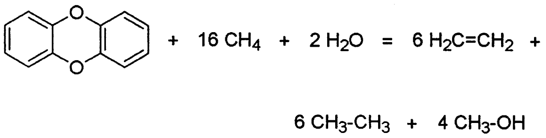
(3)

Not only bond types are conserved in these reactions but the nearest bonding environments as well. The enthalpies of formation of benzene and polychlorinated benzenes are known experimentally with an accuracy of 0.7−2.1 kJ/mol.[23] The choice of the $\Delta_f H^\circ_{298}$ value for DD is discussed below.

Since there is some doubt about the experimental enthalpies of formation of reference polychlorinated benzenes,[12] in this work their values were calculated from atomization reactions using the G3(MP2)//B3LYP composite calculation method.[21,24] The Gaussian-3 (G3) theory was presented as a way to achieve high accuracy in the predicting thermochemical data. The modification of G3 theory, referred to as G3(MP2)//B3LYP, takes significantly less computational resources compared to G3 theory with some loss in accuracy.

Results and Discussion

Dibenzo-*p*-dioxin (DD). From calorimetric measurements, the enthalpy of formation of DD first was determined as −59.2 ± 4.4 kJ/mol,[1] but recently a refined value of $\Delta_f H^\circ_{298}$ (DD) = −50.1 ± 2.2 kJ/mol appeared.[2] Since DD is the reference molecule in all isodesmic reactions used in this work (eqs 1−3), it is instructive to consider which of these two values gives better agreement with theory. For this purpose, the enthalpy of formation of DD was calculated in this work at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level using different isodesmic reactions. We started with a bond separation reaction where all formal bonds between non-hydrogen atoms in DD are separated into the simplest parent molecules containing these same kinds of linkage:



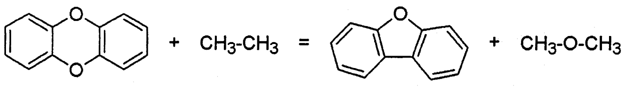
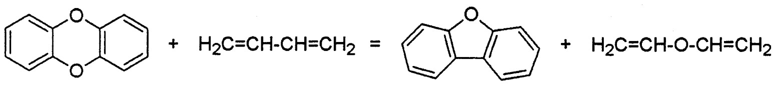
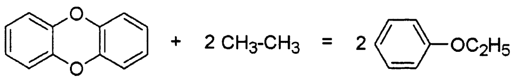
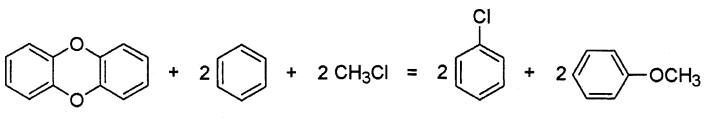
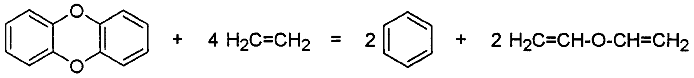
(4)

$\Delta_f H^\circ_{298}$(DD) = −46.6 kJ/mol was calculated for this reaction. The bond separation reaction has the advantage over other isodesmic reactions because of using simple reference molecules with well-recognized experimental enthalpies of formation. On the other hand, the environment of bonds in reactants and products is altered and the correlation effects are likely not well balanced. The large enthalpy change of reaction 4, $\Delta_f H^\circ_{298}$ = 727 kJ/mol, indicates that the reaction is not well balanced and therefore one would expect a large uncertainty of calculated enthalpy of formation of DD.

To construct well-balanced reactions, we selected molecules that are more similar to DD than those in reaction 4. Unfortunately, experimental data for reference molecules are not always very accurate, so we considered a sufficiently large number of reactions. The results for five reactions are given in Table 1. The experimental values of $\Delta_f H^\circ_{298}$ for species used in these reactions were taken from Pedley.[23] The average value of the enthalpy of formation of DD for these five reactions is −53.7 kJ/mol (Table 1, column "a"). Although the mean absolute deviations of calculated values from two experimental values are practically the same, the average value of −53.7 kJ/mol is slightly closer to the recent experimental value of −50.1 kJ/mol. It is obvious that such a preference for one of two experimental values is negligible because the calculated enthalpy of formation may not be accurate to better than 2−4 kJ/mol even for a well-balanced reaction.

The calculated equilibrium geometry of DD is planar. Nevertheless, the central ring is quite flexible and easily deforms to a butterfly-shaped conformation along the O···O line. The calculated harmonic vibrational frequency for this motion is very low, 37 cm^{-1}. Several other molecules in Table 1 also have low-frequency vibrations. The harmonic approximation may not be appropriate for some low-frequency modes. The rigorous treatment of the zero-point energies and thermal contributions to enthalpy requires using additional data on internal rotation and other large amplitude vibrations in molecules. For approximate treatment of molecules with low-frequency internal rotations, it was recommended to calculate the thermal component of enthalpy associated with frequencies below 260 cm^{-1} using a free rotor approximation.[14,25,26] Under such circumstances, the vibrational component of thermal contribution to enthalpy is replaced by (1/2)*RT* for each low-frequency vibration. We used this approach to evaluate the corrections for low-frequency modes. As is seen from Table 1, column "b", the average value of $\Delta_f H^\circ_{298}$ corrected for low-frequency modes, −50.3 kJ/mol, agrees closely with the recent experimental value, −50.1 kJ/mol. In addition, the application of correction for low-frequency modes decreases the mean average deviation to 3.5 kJ/mol if the experimental value of −50.1 kJ/mol is accepted, whereas the mean average deviation is increased to 8.9 kJ/mol using the experimental value of −59.2 kJ/mol.

TABLE 1: Enthalpies of Reaction and Enthalpies of Formation for Dibenzo-*p*-dioxin Calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) Level from Isodesmic Reactions and Comparison with Experimental Data (kJ/mol)[a,b]

Isodesmic reaction	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$	$\Delta_f H^\circ_{298}$
		a	b
	9	-54.05	-53.76
	-17	-51.66	-51.66
	24	-59.38	-51.06
	26	-59.09	-53.32
	-28	-44.38	-41.82
average		-53.71	-50.33
mean absolute deviation from experimental value of $\Delta_f H^\circ_{298}$(DD) = -50.1 kJ/mol [c]		5.90	3.54
mean absolute deviation from experimental value of $\Delta_f H^\circ_{298}$(DD) = -59.2 kJ/mol [d]		5.56	8.87

[a] Column a: harmonic oscillator model was used to calculate thermal corrections and ZPE. [b] Column b: free rotor approximation (see text). [c] Reference 2. [d] Reference 1.

Of the five reactions in Table 1, the significant changes in the $\Delta_f H^\circ_{298}$ values going from column "a" to column "b" occur for" the last three reactions, in which the reactants and products have different numbers of large amplitude vibrations. For example, in the third reaction the reactants have four low-frequency vibrations (DD: 37, 126, 232, 241 cm^{-1}), while the two ethoxybenzene molecules have 10 low-frequency vibrations in total (63, 112, 165, 236, 259 cm^{-1}). Contrary to the last three reactions, low-frequency correction has little effect on the $\Delta_f H^\circ_{298}$ values in the first two reactions, in which the reactants and products have similar internal rotations. Negligible change in the $\Delta_f H^\circ_{298}$ values suggests that these two reactions are especially well balanced, and one would expect a good accuracy in the calculated enthalpies of formation. The enthalpies of formations for all reference molecules in these reactions were determined with an accuracy of 0.3−1.0 kJ/mol.[23] Note, in addition to being isodesmic, the second reaction in Table 1 is the homodesmotic reaction,[16] in which there are equal numbers of C(sp^2)−H, C(sp^2)−(H)$_2$, and C(sp^2)−O bonds in the reactants and products. Due to closer matching of the hybridization states of the atoms of reactants and products as compared to isodesmic reaction, the homodesmotic reaction gives more accurate estimates of the enthalpy of formation. The average of the results for the first two reactions in Table 1, −52.8 ± 3.0 kJ/mol, is accepted in this work as the calculated enthalpy of formation of DD. In further calculations of PCDDs we used the experimental value of $\Delta_f H^\circ_{298}$(DD,gas) = −50.1 kJ/mol,[2] which is in good agreement with that calculated above.

Polychlorinated Dibenzo-*p*-dioxins (PCDDs). Enthalpies of formation of all 75 PCDD congeners were calculated at the B3LYP/6-31G(d,p) level using isodesmic reactions that are similar to those in eqs 1−3. Calculated enthalpies of formation together with the enthalpy changes of corresponding reactions are given in Table 2. The enthalpies of formation of several molecules were also calculated using the electronic energies from B3LYP/6-311+G(3df,2p) single point calculations. The $\Delta_f H^\circ_{298}$ values based on large basis calculations, −68.5 (1-CDD), −76.3 (2-CDD), −94.4 (2,3-DCDD), −130.0 (1,2,3,4-TCDD), −137.6 (2,3,7,8-TCDD), and −202.9 kJ/mol (OCDD), agree within 2.5 kJ/mol with values obtained from B3LYP/6-31G(d,p) energies (Table 2). Because of insignificant difference in two sets of values, we did not perform the time-consuming B3LYP/6-311+G(3df,2p) calculations for the remaining PCDDs.

The accurate enthalpies of formation can be calculated by the method of isodesmic reactions if the correlation errors are canceled out nearly completely by selecting reactions in which the electron correlation energy is nearly the same on both sides of the reaction. The isodesmic reactions used in this work satisfy this requirement in varying degrees. For example, among the reactions described by eqs 1−3, one would expect the most cancellation of the correlation errors for 2,3,7,8-TCDD (eq 2) because the interaction between lateral chlorine atoms and oxygen can be neglected. However, the interaction between neighboring chlorine atoms and oxygen in 1,2,3,4-TCDD (eq 1) and 1,2,3,4,6,7,8-HpCDD (eq 3) cannot be ignored. Besides, the interaction between chlorine atoms of different benzene rings may be of importance for 1,2,3,4,6,7,8-HpCDD (eq 3). Because of this, we assume that the accuracy of calculated $\Delta_f H^\circ_{298}$ values will be decreased in the series of 2,3,7,8-TCDD, 1,2,3,4-TCDD, and 1,2,3,4,6,7,8-HpCDD. As is seen from Table 2, this is in agreement with an increase of absolute values of enthalpies of reaction (19, 28, and 53 kJ/mol) for these molecules. We

TABLE 2: Enthalpies of Reaction and Enthalpies of Formation of PCDDs Calculated at B3LYP/6-31G(d,p) Level by Isodesmic Reaction Procedure (kJ/mol)

no.	isomer	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{>298}$
	Monochlorodibenzo-*p*-dioxins		
1	1	−12.1	−68.6
2	2	−4.6	−76.2
	Dichlorodibenzo-*p*-dioxins		
3	1,2	−15.2	−87.3
4	1,3	−15.8	−91.2
5	1,4	−22.6	−87.6
6	1,6	−25.1	−86.2
7	1,7	−17.7	−93.6
8	1,8	−17.9	−93.4
9	1,9	−26.7	−84.6
10	2,3	−7.9	−94.6
11	2,7	−10.2	−101.1
12	2,8	−10.3	−101.0
	Trichlorodibenzo-*p*-dioxins		
13	1,2,3	−17.9	−111.0
14	1,2,4	−25.3	−115.5
15	1,2,6	−28.7	−104.4
16	1,2,7	−21.4	−111.7
17	1,2,8	−21.7	−111.4
18	1,2,9	−30.4	−102.7
19	1,3,6	−29.8	−107.8
20	1,3,7	−22.4	−115.2
21	1,3,8	−22.5	−115.1
22	1,3,9	−31.1	−106.5
23	1,4,6	−37.8	−103.0
24	1,4,7	−29.1	−111.7
25	1,7,8	−21.8	−111.3
26	2,3,7	−14.3	−118.8
	Tetrachlorodibenzo-*p*-dioxins		
27	1,2,3,4	−27.6	−130.5
28	1,2,3,6	−32.2	−127.3
29	1,2,3,7	−24.9	−134.6
30	1,2,3,8	−25.0	−134.5
31	1,2,3,9	−33.7	−125.8
32	1,2,4,6	−41.1	−130.3
33	1,2,4,7	−32.3	−139.1
34	1,2,4,8	−32.5	−138.9
35	1,2,4,9	−41.2	−130.2
36	1,2,6,7	−32.8	−122.1
37	1,2,6,8	−34.1	−125.3
38	1,2,6,9	−42.1	−120.5
39	1,2,7,8	−26.1	−128.8
40	1,2,7,9	−35.4	−124.0
41	1,2,8,9	−34.6	−120.3
42	1,3,6,8	−35.2	−128.7
43	1,3,6,9	−43.2	−123.9
44	1,3,7,8	−27.1	−132.3
45	1,3,7,9	−36.4	−127.5
46	1,4,6,9	−51.2	−119.1
47	1,4,7,8	−33.8	−128.8
48	2,3,7,8	−18.8	−136.1
	Pentachlorodibenzo-*p*-dioxins		
49	1,2,3,4,6	−43.8	−144.9
50	1,2,3,4,7	−35.2	−153.5
51	1,2,3,6,7	−36.9	−144.4
52	1,2,3,6,8	−38.3	−147.5
53	1,2,3,6,9	−46.1	−142.9
	Pentachlorodibenzo-*p*-dioxins		
54	1,2,3,7,8	−30.0	−151.3
55	1,2,3,7,9	−39.4	−146.4
56	1,2,3,8,9	−38.3	−143.0
57	1,2,4,6,7	−45.7	−147.5
58	1,2,4,6,8	−47.1	−150.6
59	1,2,4,6,9	−55.0	−145.9
60	1,2,4,7,8	−37.6	−155.6
61	1,2,4,7,9	−47.0	−150.7
62	1,2,4,8,9	−45.9	−147.3
	Hexachlorodibenzo-*p*-dioxins		
63	1,2,3,4,6,7	−48.8	−161.7
64	1,2,3,4,6,8	−50.0	−165.0
65	1,2,3,4,6,9	−57.9	−160.3
66	1,2,3,4,7,8	−40.7	−169.8
67	1,2,3,6,7,8	−41.4	−166.3
68	1,2,3,6,7,9	−50.2	−169.4
69	1,2,3,6,8,9	−50.3	−169.3
70	1,2,3,7,8,9	−42.5	−165.2
71	1,2,4,6,7,9	−59.0	−172.5
72	1,2,4,6,8,9	−59.1	−172.4
	Heptachlorodibenzo-*p*-dioxins		
73	1,2,3,4,6,7,8	−53.5	−183.4
74	1,2,3,4,6,7,9	−62.4	−186.4
	Octachlorodibenzo-*p*-dioxin		
75	1,2,3,4,6,7,8,9	−65.8	−200.3

propose the following scheme for estimating uncertainties of the calculated $\Delta_f H^\circ_{298}$ values depending on the $\Delta_r H^\circ_{298}$ values:

$\Delta_r H^\circ_{298}$, kJ/mol	uncertainty in $\Delta_f H^\circ_{298}$, kJ/mol
5−15	4−8
15−30	8−15
30−65	15−30

The low $\Delta_r H^\circ_{298}$ values for 2-CDD (−5 kJ/mol) and 2,3-DCDD (−8 kJ/mol) show that the corresponding isodesmic reactions are especially well-balanced reactions, which are almost thermoneutral. The correlation errors are canceled out nearly completely for 2-CDD and 2,3-DCDD, and this suggests good accuracy for the calculated enthalpies of formation. Since the experimental data are available for these compounds, it is of interest to compare the experimental and calculated values. The value of $\Delta_f H^\circ_{298}$(2-CDD) = −74.1 ± 3.3 kJ/mol determined from calorimetric measurements[4] is in excellent agreement with calculated value of −76 ± 4 kJ/mol. As for 2,3-DCDD, the experimental value, −111.9 ± 6.9 kJ/mol,[5] is substantially more negative than calculated one, −95 ± 5 kJ/mol. Note the uncertainty of the experimental value is rather large.

The experimental enthalpy of formation of 1-CDD (−88.2 ± 4.8 kJ/mol)[3] is also distinctly lower than the calculated value (−69 ± 8 kJ/mol). The monochlorodibenzo-*p*-dioxins are worthy of special attention. According to calorimetric data,[3,4] 1-CDD is the more stable and hence more abundant isomer than 2-CDD. However, this is in conflict with the experimental data on the relative concentrations of 1- and 2-CDD[27] and with the relative stability of the two isomers calculated in this work, so we are inclined to believe that the available experimental $\Delta_f H^\circ_{298}$ values are not sufficiently reliable. Notice that considerable uncertainties in the experimental enthalpies of formation for chlorinated organic compounds are often the case due to incomplete combustion in calorimetric measurements.

As in the case of DD, we tried to improve the agreement between experimental and calculated enthalpies of formation by corrections for low-frequency modes. However, for PCDDs there are similar structures on both sides of the reaction (eqs 1−3) and errors associated with large amplitude motions are canceled out almost completely. We used the harmonic oscillator treatment for all PCDDs because of little effect of low-frequency corrections on calculated $\Delta_f H^\circ_{298}$ values.

It is interesting to compare the calculated $\Delta_f H^\circ_{298}$ values of PCDDs with those estimated earlier by group additivity and semiempirical calculations. Enthalpies of formation calculated by Saito and Fuwa using the semiempirical molecular orbital method PM3[11] are in rather good agreement with $\Delta_f H^\circ_{298}$ values calculated in this work. For DD ($\Delta_f H^\circ_{298}$ = −40.2 kJ/mol) and some PCDD isomers, the PM3 enthalpies of formation are about 10 kJ/mol higher than those in Table 2, whereas the $\Delta_f H^\circ_{298}$ values for the remaining isomers and the trend in their change are close for both sets of data (Figure 1). The $\Delta_f H^\circ_{298}$ values estimated using the group additivity approach[6,9] are appreciably lower than those calculated in this work.

Recently Leon et al.[12] calculated the enthalpies of formation of 10 PCDDs using the density functional method at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level of theory. Pointing to the conflicting $\Delta_f H^\circ_{298}$ values for polychlorinated benzenes, the authors proposed alternative isodesmic reactions in which only monochlorobenzene was used as reference. In other words, instead of reaction 3, the following reaction was used to calculate the enthalpy of formation of 1,2,3,4,6,7,8-HpCDD:

The advantage of the isodesmic reaction 5 is that the enthalpies of formation of all reference molecules are well-known, while the uncertainty in the experimental values for tri- and tetrachlorobenzenes used in eq 3 might be much more than that recommended by Pedley[23] (1 kJ/mol). However, using the isodesmic reactions 1−3 should benefit from better cancellation of correlation errors in the B3LYP calculations, because not only bond types are conserved in our reactions, but the similar

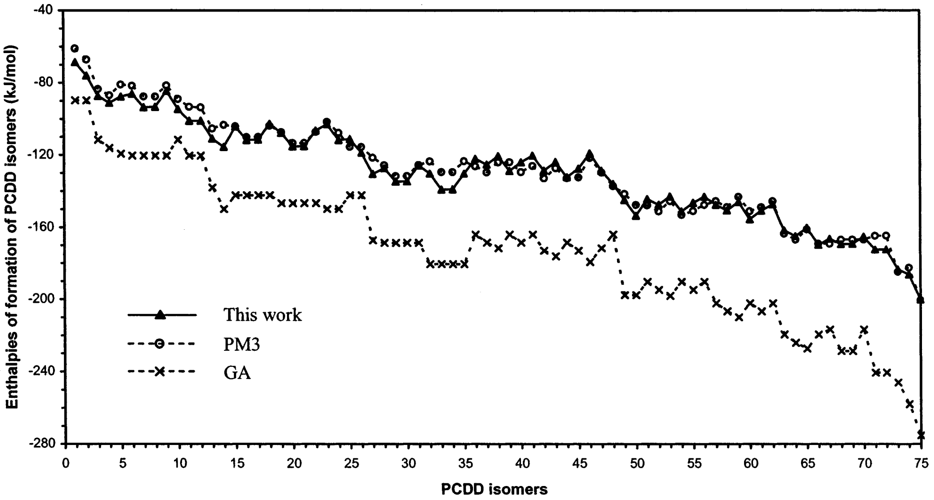
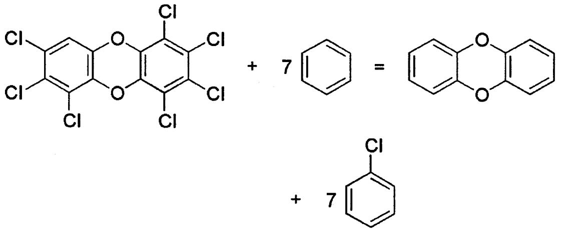


Figure 1. Comparison of enthalpies of formation of PCDD isomers calculated in this work and by the semiempirical PM3[11] and group additivity[9] methods. The numbers on the abscissa correspond to the PCDD numbers in Table 2.

TABLE 3: Comparison of Enthalpies of Formation and Enthalpies of Reaction of PCDDs Calculated Using Different Types of Isodesmic Reactions (kJ/mol)

molecule	isodesmic reactions with monochlorobenzene as reference[a] Leon et al.[b] $\Delta_f H^\circ_{298}$	$\Delta_r H^\circ_{298}$	isodesmic reactions with polychlorinated benzenes as reference[c] this work $\Delta_f H^\circ_{298}$	$\Delta_r H^\circ_{298}$
1-CDD	−78.7 ± 4.6	−11	−69 ± 8	−12
2-CDD	−85.9 ± 4.6	−4	−76 ± 5	−5
2,3-DCDD	−100.9 ± 4.9	−19	−95 ± 5	−8
2,3,7,8-TCDD	−140.6 ± 5.3	−41	−136 ± 10	−19
1,2,3,7,8-PnCDD	−145.1 ± 5.5	−67	−151 ± 15	−30
1,2,3,4,7,8-HxCDD	−148.0 ± 5.7	−95	−170 ± 20	−41
1,2,3,6,7,8-HxCDD	−149.5 ± 5.7	−93	−166 ± 20	−41
1,2,3,7,8,9-HxCDD	−148.6 ± 5.7	−94	−165 ± 20	−43
1,2,3,4,6,7,8-HpCDD	−151.4 ± 5.9	−122	−183 ± 25	−53
OCDD	−153.4 ± 6.1	−150	−200 ± 30	−67

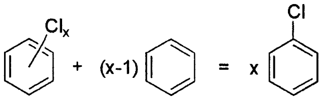
[a] Reactions like eq 5. [b] $\Delta_f H^\circ_{298}$ values were taken from Table 7 (isodesmic reaction 7) in ref 12. $\Delta_r H^\circ_{298}$ values were calculated using data from Table 5 in ref 12. [c] Reactions like eqs 1−3.



(5)

bonding environment as well. In addition, reaction 5 includes 16 molecules as compared with 6 molecules in reaction 3. The error of 1.3 kJ/mol in the enthalpy of formation for each monochlorobenzene molecule could result in an error of 9 kJ/mol in the estimated enthalpy of formation of 1,2,3,4,6,7,8-HpCDD. The discrepancies in the $\Delta_f H^\circ_{298}$ values calculated using different types of the isodesmic reactions are shown in Table 3. More negative enthalpies of formation of 1-CDD and 2-CDD calculated by Leon et al.[12] result from using the early experimental value of $\Delta_f H^\circ_{298}(\mathrm{DD}) = -59.2$ kJ/mol.[1] As would be expected, the most discrepancies occur for PCDDs with 1,2,3-trichloro- and 1,2,3,4-tetrachlorobenzene fragments. The lack of group balance in reactions such as eq 5 results in large absolute values of enthalpies of reaction $\Delta_r H^\circ_{298}$ (41−150 kJ/mol). The enthalpies of reaction for eqs 1−3 are less than 70 kJ/mol, indicating more similar structures on both sides of the equations and suggesting more reasonable cancellation of errors.

Assuming large uncertainties in the experimental enthalpies of formation of polychlorinated benzenes, Leon et al.[12] estimated their values from DFT calculations using isodesmic reaction 6:



(6)

The calculated values differ significantly from the experimental values for tri-, tetra-, penta-, and hexachlorobenzenes (Table 4). Leon et al.[12] believe that these discrepancies are due to incorrect experimental values. We think that reaction 6, as well as reaction 5, underestimate the interactions between chlorine atoms and the errors in the calculated $\Delta_f H^\circ_{298}$ values are many times larger than those given in Table 4.

Leon et al.[12] also calculated the enthalpies of formation of PCDDs using eqs 1−3 together with the calculated $\Delta_f H^\circ_{298}$ values for polychlorinated benzenes. Since the combination of reactions 3 and 6 leads to reaction 5, it is not surprising that in this case the calculated values of $\Delta_f H^\circ_{298}$(PCDDs) are practically the same as obtained by Leon et al.[12] for isodesmic reactions such as eq 5 (Table 3).

To check the reliability of the experimental $\Delta_f H^\circ_{298}$ values of polychlorinated benzenes, in this work their values were calculated by atomization procedure at the G3(MP2)//B3LYP level. The results of our calculations are shown in Table 4 and Figure 2. The distinctions between two sets of calculated values

TABLE 4: Experimental and Calculated Enthalpies of Formation of Polychlorinated Benzenes (kJ/mol)

	experimental			calculated	
molecule[a]	Platonov et al.[b]	Pedley[c]	Yan et al.[d]	B3LYP from isodesmic reactions 6 Leon et al.[e]	G3(MP2)//B3LYP from atomization reactions this work
chlorobenzene	54.3 ± 1.3	52.0 ± 1.3			42.6
1,2-dichlorobenzene	33.9 ± 3.1	30.2 ± 2.1		34.0 ± 2.0	17.4
1,3-dichlorobenzene	29.5 ± 1.8	25.7 ± 2.1		24.6 ± 2.0	11.6
1,4-dichlorobenzene	25.7 ± 1.3	22.5 ± 1.5		24.8 ± 2.0	11.9
1,2,3-trichlorobenzene	−1.7 ± 2.2	3.8 ± 0.7	8.2 ± 1.8	19.2 ± 2.5	−5.8
1,2,4-trichlorobenzene	−8.8 ± 1.8	−8.1 ± 1.0	4.9 ± 1.6	9.1 ± 2.5	−11.5
1,3,5-trichlorobenzene	−13.0 ± 3.6	−13.4 ± 1.0	−2.6 ± 1.4	0.6 ± 2.5	−16.7
1,2,3,4-tetrachlorobenzene	−26.8 ± 3.5	−25.4 ± 1.0		6.2 ± 2.9	−27.3
1,2,3,5-tetrachlorobenzene	−35.3 ± 3.7	−34.9 ± 1.0		−3.4 ± 2.9	−32.6
1,2,4,5-tetrachlorobenzene	−37.5 ± 3.0	−32.6 ± 0.8		−4.8 ± 2.9	−33.0
pentachlorobenzene	−40.0 ± 8.7	−40.0 ± 8.7		−5.9 ± 3.2	−47.2
hexachlorobenzene	−56.2 ± 8.5	−35.5 ± 9.3		−4.5 ± 3.5	−59.8

[a] Reference molecules used for calculating the enthalpies of formation of PCDDs are in italics. [b] Reference 28. [c] Reference 23. [d] Reference 29. [e] Reference 12.

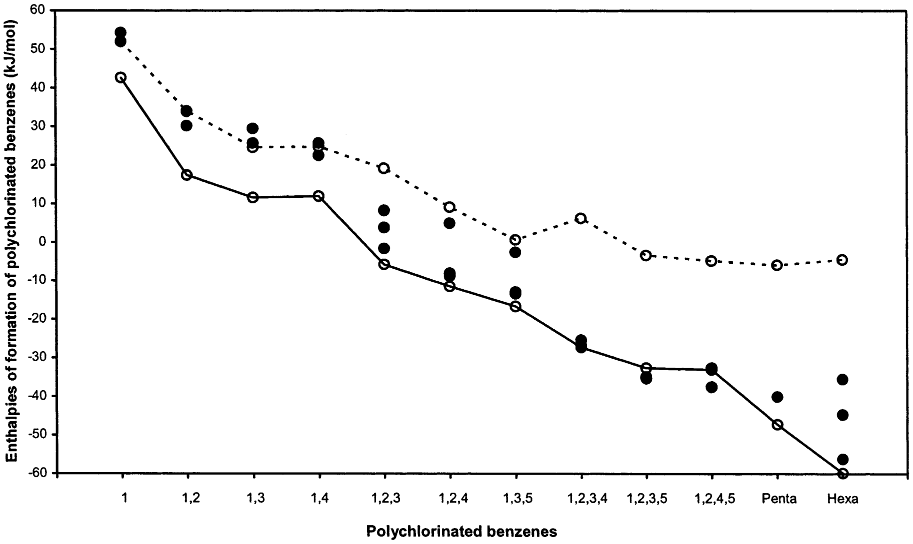


Figure 2. Comparison of experimental and calculated enthalpies of formation of polychlorinated benzenes. The solid circles are the experimental data from refs 23, 28, and 29. The open circles connected by the dashed line are the values calculated at the B3LYP level by Leon et al.[12] The open circles connected by the solid line are the G3(MP2)//B3LYP values calculated in this work.

acquire significance starting with 1,3,5-trichlorobenzene: the $\Delta_f H^\circ_{298}$ values calculated by Leon et al.[12] vary only slightly and the enthalpy of formation of 1,2,3,4-tetrachlorobenzene is even higher than that of 1,3,5-trichlobenzene, whereas G3(MP2)//B3LYP values become substantially more negative when the number of chlorine atoms increases. An unexpectedly high value of $\Delta_f H^\circ_{298}$(1,2,3,4-tetrachlorobenzene) is responsible for much less negative enthalpies of formation of highly chlorinated PCDDs calculated by Leon et al.[12] compared to our values (Table 3).

Due to uncertainty in the experimental enthalpies of formation of polychlorinated benzenes, it is difficult to evaluate the error of G3(MP2)//B3LYP values. It can be seen from Table 4 and Figure 2 that the G3(MP2)//B3LYP enthalpies of formation of mono-, di-, and 1,2,3-trichlorobenzene are underestimated by 9−18 kJ/mol. If this trend will be conserved in going from tri- to tetrachlorobenzenes, one might expect less negative values of enthalpies of formation for 1,2,4-tri- and 1,2,3,4-tetrachlorobenzene in comparison with those recommended by Pedley[23] and accepted in this work. Unfortunately, only accurate experimental data can either validate or disprove this assumption. The G3(MP2)//B3LYP results for benzenes with four and more chlorine atoms can be considered only as rough estimates. An accumulation of errors in the application of G2 theory to larger molecules has been observed in this procedure,[13] and the same trend might be expected for G3 theory. Nevertheless, the G3(MP2)//B3LYP results indicate that the difference between the $\Delta_f H^\circ_{298}$ values of 1,2,4-tri- and 1,2,3,4-tetrachlorobenzene is more likely to be larger than was estimated by Leon et al.[12]

From the above discussion it appears that the $\Delta_f H^\circ_{298}$ values of polychlorinated benzenes and PCDDs were obtained by Leon et al.[12] from not well-balanced reactions and their values may be somewhat overestimated. It is also doubtful that the relative stability of PCDDs with five to eight chlorine atoms is practically the same. Although we suppose that the values obtained in this work from isodesmic reactions 1−3 (Table 2) are more reasonable, it must not be ruled out that the $\Delta_f H^\circ_{298}$ values of some highly chlorinated PCDDs are more positive by 5−15 kJ/mol than those in Table 2.

Conclusions

With recent development of techniques of ab initio theory and computer hardware, it has become possible to determine the thermochemical properties of small to medium-sized molecules with high accuracy. However, such calculations are of high computational cost and are not sufficiently advanced for large polychlorinated molecules. For this reason, an active interest in the applicability of DFT calculations for estimating thermochemical properties of large molecules would remain as before. In this work the enthalpies of formation of gaseous DD and PCDDs were calculated based on B3LYP calculations and using the method of isodesmic reactions. As is seen, the accuracy of results is comparable with experiment, considering the often large uncertainties of the calorimetric $\Delta_f H^\circ_{298}$ values for chlorinated organic compounds.

The problem in the application of isodesmic procedure to PCDDs is that the calculated $\Delta_f H^\circ_{298}$ values are highly dependent on the choice of isodesmic reactions. The cancellation of calculation errors might be insufficient for reactions in which the nearest environment of atoms is not conserved in the reactants and products. Large uncertainties would be expected for such reactions, especially for highly chlorinated isomers. Reasonable cancellation of errors is suggested for reactions with similar structures on both sides of the equations. However, in this case the accuracy of the $\Delta_f H^\circ_{298}$(PCDDs) values is dictated by the uncertainties of the experimental enthalpies of formation of tri- and tetrachlorobenzenes. We believe that the errors in experimental values do not exceed 10 kJ/mol, and thus our results are favored over those obtained from isodesmic reactions using only monochlorobenzene as reference compound.

Acknowledgment. This research was supported by the Russian Foundation for Basic Research under Grant No. 02-03-32227.

Supporting Information Available: Tables of electronic energies at different levels of theory, zero-point energies, and thermal corrections together with experimental values of enthalpies of formation for all molecules used in isodesmic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lukyanova, V. A.; Kolesov, V. P.; Avramenko, N. V.; Vorobieva, V. P.; Golovkov, V. F. *Zh. Fiz. Khim.* **1997**, *71*, 406.

(2) Pimenova, S. M.; Melkhanova, S. V.; Kolesov, V. P.; Demyanov, P. I.; Fedotov, A. N.; Vorobieva, V. P. *J. Chem. Thermodyn.* **2002**, *34*, 385.

(3) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chernov, C. A.; Vorobieva, V. P. *Zh. Fiz. Khim.* **1998**, *72*, 7.

(4) Papina, T. S.; Kolesov, V. P.; Vorobieva, V. P.; Golovkov, V. F. *J. Chem. Thermodyn.* **1996**, *28*, 307.

(5) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Golovkov, V. F.; Chernov, C. A.; Vorobieva, V. P. *J. Chem. Thermodyn.* **1998**, *30*, 431.

(6) Shaub, W. M. *Thermochim. Acta* **1982**, *55*, 59.

(7) Thompson, D. *Chemosphere* **1994**, *29*, 2545.

(8) Thompson, D.*Thermochim. Acta* **1995**, *261*, 7.

(9) Dorofeeva, O. V.; Iorish, V. S.; Moiseeva, N. F. *J. Chem. Eng. Data* **1999**, *44*, 516.

(10) Koester, C. J.; Hites, R. A. *Chemosphere* **1988**, *17*, 2355.

(11) Saito, N.; Fuwa, A. *Chemosphere* **2000**, *40*, 131.

(12) Leon, L. A.; Notario, R.; Quijano, J.; Sanchez, C. *J. Phys. Chem. A* **2002**, *106*, 6618.

(13) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(15) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(16) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Theor. Chim. Acta* **1975**, *38*, 121.

(17) Lay, T. H.; Krasnoperov, L. N.; Venanzi, C. A.; Bozzelli, J. W.; Shokhirev, N. V. *J. Phys. Chem.* **1996**, *100*, 8240.

(18) Chen, Z. X.; Xiao, J. M.; Xiao, H. M.; Chiu, Y. N. *J. Phys. Chem. A* **1999**, *103*, 8062.

(19) Wang, L.; Zhang, J. *J. Mol. Struct. (THEOCHEM)* **2002**, *581*, 129.

(20) Zhu, L.; Bozzelli, J. W. *J. Phys. Chem. A* **2002**, *106*, 345.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1997**, *270*, 419.

(23) Pedley J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. I.

(24) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650.

(25) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(26) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(27) Bacher, R.; Swerew, M.; Ballschmiter, K. *Environ. Sci. Technol.* **1992**, *26*, 1649.

(28) Platonov, V. A.; Simulin, Yu. N.; Rosenberg, M. M. *Russ. J. Phys. Chem.* **1985**, *59*, 814.

(29) Yan, H.; Gu, J.; An, X.; Hu, R. *Huaxue Xuebao* **1987**, *45*, 1184; *NIST Chemistry Webbook*: http://webbook.nist.gov/chemistry/.

(30) Raghavari, K.; Stefanov, B. B.; Curtiss, L. A. *J. Chem. Phys.* **1997**, *106*, 6764.