

COMPUTATIONAL PREDICTION OF THE HEATS OF FORMATION FOR GASOUS FLUORO- AND CHLOROBENZENES BY APPLYING ISODESMIC APPROACH

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Introduction

The availability of thermodynamic properties of chlorinated hazardous waste materials such as 2,3,7,8-tetrachlorodibenzo-p-dioxin is of fundamental significance for understanding their behavior under various conditions during the process of incineration. The heats of formation for chlorinated benzenes are necessarily important to estimate those of polychlorinated dibenzo-p-dioxins and dibenzofurans by group additivity approach or by semi-empirical and *ab initio* molecular orbital calculations. In the present paper, we have estimated the heats of formation for gaseous fluoro- and chlorobenzenes by applying isodesmic approach in *ab initio* molecular orbital calculations, and compared theoretical values thus obtained with experimental ones.

Methods

All molecular orbital calculations were conducted with the Gaussian 98 code.¹⁾ The energies of benzene (C₆H₆), fluorobenzenes (C₆H₅F-C₆F₆), and chlorobenzenes (C₆H₅Cl-C₆Cl₆) were estimated for the isodesmic approach by the G2MP2 methodology²⁾ and a density functional method.

Molecular structures were determined in the density functional method by using the 6-311G(d,p) basis set and Becke's three-parameter nonlocal exchange functional³⁾ in conjunction with the nonlocal correlation functional of Lee et al.⁴⁾ (B3LYP). Energies were obtained at the B3LYP/6-311+G(3df,2p) level of theory.

The heats of formation of C₆H₅F and C₆H₅Cl have been estimated using the isodesmic reactions of C₆H₆+CH₃X=C₆H₅X+CH₄ (X=F and Cl) by the G2 methodology.⁵⁾

Results and Discussion

We have considered isodesmic reactions listed in Table 1 to predict the heats of formation for fluorobenzenes and chlorobenzenes. There is more than one isodesmic reaction other than listed in the same table that may be constructed to predict a heat of formation of interest (e.g. 1,2,4-C₆H₄X₂ + C₆H₅X = 1,2,4,5-C₆H₂X₄ + C₆H₆, and so on). It is noteworthy that isodesmic reaction in this system gave nearly the same values within errors less than 0.2 kJmol⁻¹ for the heat of formation. The reactions chosen are ones with the smallest value for ΔH.

As is shown in Table 1, the reactions are all exothermic for both fluorobenzenes and chlorobenzenes. *Ortho* substitution reactions gave larger values for ΔH than *meta* and *para* substitution reactions.

For fluorobenzenes, computed values of ΔH for the reactions are consistent by the G2MP2 and the density functional method. The heat of formation for C₆H₅F were determined by the G2 method using the isodesmic reaction of C₆H₆ + CH₃F = C₆H₅F + CH₄. The heat of formation for C₆H₆ is assumed to be experimental value of 82.8 kJmol⁻¹.⁶⁾ Those for CH₄ and CH₃F are cited from Ref. 7. The heat of formation, thus obtained, for C₆H₅F are -112.2 kJmol⁻¹.

Table 1 $\Delta H^\circ_{298K}(\text{kJmol}^{-1})$ for isodesmic reactions

Isodesmic reactions	X=F		X=Cl		Exp. ⁸⁾
	G2MP2	B3LYP	G2MP2	B3LYP	
$\text{C}_6\text{H}_5\text{X}+\text{C}_6\text{H}_5\text{X}=1,2\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_6$	+18.7	+19.1	+9.1	+12.8	+8.2
$\text{C}_6\text{H}_5\text{X}+\text{C}_6\text{H}_5\text{X}=1,3\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_6$	+3.0	+3.0	+2.7	+3.3	+3.8
$\text{C}_6\text{H}_5\text{X}+\text{C}_6\text{H}_5\text{X}=1,4\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_6$	+6.4	+5.9	+3.4	+3.4	0
$1,2\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_5\text{X}=1,2,3\text{-C}_6\text{H}_3\text{X}_3+\text{C}_6\text{H}_6$	+20.4	+21.3	+11.3	+15.9	-7.0
$1,2\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_5\text{X}=1,2,4\text{-C}_6\text{H}_3\text{X}_3+\text{C}_6\text{H}_6$	+8.0	+8.0	+5.0	+5.8	-14.1
$1,3\text{-C}_6\text{H}_4\text{X}_2+\text{C}_6\text{H}_5\text{X}=1,3,5\text{-C}_6\text{H}_3\text{X}_3+\text{C}_6\text{H}_6$	+6.7	+6.3	+5.6	+6.7	-13.9
$1,2,3\text{-C}_6\text{H}_3\text{X}_3+\text{C}_6\text{H}_5\text{X}=1,2,3,4\text{-C}_6\text{H}_2\text{X}_4+\text{C}_6\text{H}_6$	+25.6	+25.8	+13.1	+17.7	+3.5
$1,2,3\text{-C}_6\text{H}_3\text{X}_3+\text{C}_6\text{H}_5\text{X}=1,2,3,5\text{-C}_6\text{H}_2\text{X}_4+\text{C}_6\text{H}_6$	+11.0	+10.8	+6.9	+8.2	-5.0
$1,2\text{-C}_6\text{H}_4\text{X}_2+1,2\text{-C}_6\text{H}_4\text{X}_2=1,2,4,5\text{-C}_6\text{H}_2\text{X}_4+\text{C}_6\text{H}_6$	+15.4	+15.0	+8.8	+10.1	-22.4
$1,2,3,4\text{-C}_6\text{H}_2\text{X}_4+\text{C}_6\text{H}_5\text{X}=\text{C}_6\text{HX}_5+\text{C}_6\text{H}_6$	+27.9	+28.6	+14.4	+19.6	+15.4
$\text{C}_6\text{HX}_5+\text{C}_6\text{H}_5\text{X}=\text{C}_6\text{X}_6+\text{C}_6\text{H}_6$	+45.2	+46.3	+22.7	+32.4	+12.4

 B3LYP^a: B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p)

 Table 2 Calculated and experimental $H^\circ_{298K}(\text{kJmol}^{-1})$ of fluoro- and chlorobenzenes

Species	X=F			X=Cl		
	G2MP2	B3LYP ^a	Exp.	G2MP2	B3LYP ^a	Exp.
C_6H_6	(82.8)	(82.8)	82.8 ⁶⁾	(82.8)	(82.8)	82.8 ⁶⁾
$\text{C}_6\text{H}_5\text{X}$	[-112.2]	[-112.2]	-116.0 ⁹⁾	[+46.4]	[+46.4]	+54.3 ⁸⁾ +50.9 ¹⁰⁾
$1,2\text{-C}_6\text{H}_4\text{X}_2$	-288.5	-288.1	-293.8 ¹²⁾	+19.1	+22.8	+33.9 ⁸⁾ +29.6 ¹¹⁾
$1,3\text{-C}_6\text{H}_4\text{X}_2$	-304.2	-304.2	-309.2 ¹²⁾	+12.7	+13.3	+29.5 ⁸⁾ +25.8 ¹¹⁾
$1,4\text{-C}_6\text{H}_4\text{X}_2$	-300.8	-301.3	-306.7 ¹²⁾	+13.4	+13.4	+25.7 ⁸⁾ +22.2 ¹³⁾
$1,2,3\text{-C}_6\text{H}_3\text{X}_3$	-463.4	-461.8		-6.0	+2.3	-1.7 ⁸⁾
$1,2,4\text{-C}_6\text{H}_3\text{X}_3$	-475.5	-475.1		-12.3	-7.8	-8.8 ⁸⁾
$1,3,5\text{-C}_6\text{H}_3\text{X}_3$	-492.5	-492.9		-18.1	-16.4	-13.0 ⁸⁾
$1,2,3,4\text{-C}_6\text{H}_2\text{X}_4$	-632.8	-631.0		-29.3	-16.4	-26.8 ⁸⁾
$1,2,3,5\text{-C}_6\text{H}_2\text{X}_4$	-647.4	-646.0		-35.5	-25.9	-35.3 ⁸⁾
$1,2,4,5\text{-C}_6\text{H}_2\text{X}_4$	-644.4	-644.0	-646.8 ¹⁴⁾	-35.8	-27.1	-37.5 ⁸⁾
C_6HX_5	-799.9	-797.4	-807.5 ¹⁵⁾	-51.3	-33.2	-40.0 ⁸⁾
C_6X_6	-949.7	-946.1	-955.6 ¹⁶⁾	-65.0	-37.2	-56.2 ⁸⁾

 B3LYP^a: B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p)

By using these values, the heats of formation of $C_6H_4F_2$ - C_6F_6 were successively determined. As is shown in Table 2, computed values for the heats of formation for $C_6H_4F_2$ - C_6F_6 are in good agreement with experimental values.

For chlorobenzenes, as is shown in Table 1, the values for ΔH are somewhat different in the two methods, especially for *ortho* substitution reactions. The B3LYP method gave larger values for ΔH by 4~5 kJmol^{-1} than the G2MP2 method. Due to experimental values by Platonov et al.⁸⁾ for the heats of formation for chlorobenzenes, ΔH for the reactions seems to change irregularly.

The G2MP2 method was found to give better results in isodesmic approach to predict the heats of formation for CH_2Cl_2 , $CHCl_3$, and CCl_4 than the B3LYP method, so the former is considered to be more reliable than the latter in this system. The heat of formation for C_6H_5Cl was determined to be 46.4 kJmol^{-1} by the same procedure as for C_6H_5F using the isodesmic reaction of $C_6H_6 + CH_3Cl = C_6H_5Cl + CH_4$. This value is somewhat different from the experimental values of 50.9 and 54.3 kJmol^{-1} . The heats of formation obtained for $C_6H_4Cl_2$ - C_6Cl_6 are listed in Table 2. The results of the present theoretical calculations are in somewhat conflict with the experimental ones by Platonov et al.

The magnitude for the heat of formation for C_6H_5Cl is key quantity in this successive isodesmic approach to predict those for the series of chlorobenzenes, so further detail investigation for C_6H_5Cl is required and is in progress. It is noted, however, that the whole agreement from $C_6H_4Cl_2$ through C_6Cl_6 between the present calculations and the experiment by Platonov et al. is not attained as far as the value of the heat of formation for C_6H_5Cl is taken as the sole parameter. Further theoretical and experimental investigation is needed.

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