

# Predicting the heat of formation of chlorinated phenols and associated chlorine isotopologues

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## Abstract

Using quantum chemical techniques, the standard gas-phase enthalpies of formation of chlorinated phenols were calculated by two high level composite methods. The standard Gibbs free energies of formation of the chlorinated phenols were also estimated. The results are compared to experimental and other theoretical studies and generally good agreement between experiments and model prediction is found. We subsequently assess the influence of the position of chlorine in the aromatic ring and isotope fractionation caused by <sup>37</sup>Cl on the heat of formation of a series of polychlorinated phenols.

*Keywords: Dioxins, Thermodynamic data, Isotope effect, Heat of formation*

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## Introduction

Chlorinated aromatics, and especially the notorious group of compounds known as dioxins (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans), are hazardous to human health [1, 2]. It is well established that they are produced in a wide range of combustion processes, including incineration, thermal handling of waste and in some metallurgical systems. Incomplete combustion, salient temperature conditions and the presence of chlorinated compounds in the combustion media are all important influences on their formation [2].

Knowledge of the heat of formation (i.e., its standard enthalpy of formation at 1 bar and 298.15 K) is an important parameter for understanding the behaviour of a compound during chemical reaction. Experimental measurements of heat of formation of chlorinated aromatic compounds have been influenced by sample impurities and uncertainties in measurement of enthalpy change accompanied with phase transitions. As a result, experimental estimates of the enthalpy of formation of chlorinated aromatic compounds have large uncertainties and the agreement between different studies is generally poor [3, 4].

Investigating the effect caused by heavier stable isotopes is a well-established, proven experimental technique, used to trace the sources and sinks of organic pollutants in the environment [5]. Isotope fractionation results from the small difference in the mass of the isotopes of the same element. Since the electronic activity plays the key role in determining the properties of the molecule and as isotopes have virtually identical electronic structures, isotopologues, molecules which differ only in their isotopic composition, generally have very small but measurable differences in their properties. The changes caused by each isotope are proportional to the relative mass difference [5].

In our research, we are undertaking high level theoretical calculations to specify standards by which we can determine the sources and mechanisms of formation of dioxin and dioxin precursors by measuring the <sup>37</sup>Cl/<sup>35</sup>Cl, <sup>13</sup>C/<sup>12</sup>C, <sup>18</sup>O/<sup>16</sup>O ratios. In this paper we chose <sup>37</sup>Cl isotope because of its high relative abundance (24.23%) and we focus on its influence on the stability of chlorinated phenols.

## Methodology

All calculations were conducted using Gaussian 03 at the Australian Centre of Advanced Computing and Communications (ac3) and Gaussian 09 at the National Computational Infrastructure (NCI). Two high accuracy composite methods were employed, CBS-QB3 and G4-MP2. CBS-QB3 was developed from the complete basis set family (CBS-Q) by calculating the optimised geometries and frequencies using the hybrid DFT of B3LYP. B3LYP employs the three parameter Becke exchange functional B3 with the Lee–Yang–Parr nonlocal correctional functional LYP, along with the basis set 6-311G(2d,d,p) in place of MP2 optimisation. Another feature of CBS-QB3 is the replacement of QCISD(T) by CCSD(T) and the inclusion of atomic spin–orbit interactions. CBS-QB3 provides a total average error of approximately 0.8 kJ/mol [6].

G4-MP2 on the other hand is essentially a simplification of G4, in which the MP2 method replaces MP3 and MP4 large basis set calculations to save computation time at the expense of some loss in accuracy. G4-MP2 records an average absolute deviation of 4.2 kJ/mol for the G3/05 test set which makes it economically attractive and is suitable for a wide range of calculations [7].

## Results and Discussion

When studying chlorinated phenols, calculations must discriminate between the two *ortho* and the *meta*

positions due to the considerable differences in the heat of formation for these compounds. These differences are caused mainly by the intramolecular hydrogen bond between the hydrogen atom in the hydroxyl group and the nearby chlorine atom. Throughout this paper, the hydroxyl group is taken to point toward the number 2 carbon in the aromatic ring. This convention of reporting stereoisomers results in *syn*-2-chlorophenol to be equivalent to 2-chlorophenol, and *anti*-2-chlorophenol to correspond to 6-chlorophenol.

The rotational barrier between the 2,3-dichlorophenol and 5,6-dichlorophenol was predicted to be 11.1 kJ/mol by a single transition state calculated for the 180° rotation using B3LYP method, along with 6-311+G(2d,p) basis set as illustrated in Figure 1. Table 1 shows the predicted intramolecular hydrogen bond strengths for chlorinated phenols using the four composite methods. Note that only molecules with adjacent chlorine atoms were considered. For example, trichlorophenol denotes the difference between 2,3,4-trichlorophenol and 4,5,6-trichlorophenol.

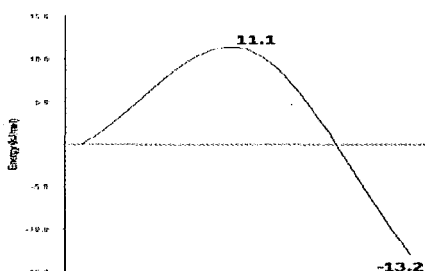


Figure 1: Rotational barrier between 2,3-dichlorophenol and 5,6-dichlorophenol.

Table 1: Hydrogen bond strength estimated by different methods (kJ/mol).

	G4-MP2 <sup>a</sup>	CBS-QB3 <sup>a</sup>	G3X <sup>b</sup>	G3X-MP2 <sup>b</sup>
Chlorophenol	13.12	13.02	13.3	13.3
Dichlorophenol	13.50	13.64	13.4	10.7
Trichlorophenol		13.64	12.7	11.9
Tetrachlorophenol		13.29	13.2	13.3

a: Calculated in this work, b: Calculated by Wang et al. [8]

### A. Enthalpies of Formation of Chlorinated Phenols

In the estimation of the heat of formation, quantum chemical calculations supported by isodesmic reactions were employed in order to reduce error. In this procedure, a hypothetical isodesmic reaction is proposed in which all the heats of formation for all reactants and products (except the target compound) are accurately known. In this paper, the reaction of phenol with the appropriate chlorinated benzene to form benzene and the targeted chlorophenol was used. The heat of reaction is then estimated by one of the high accuracy methods. In this paper, CBS-QB3 and G4-MP2 composite methods were employed. Figure 2 illustrates an example of an isodesmic reaction deployed in this paper. Table 2 shows the experimental heats of formation used in the isodesmic reaction.

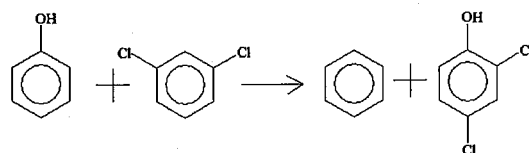


Figure 2: The isodesmic reaction deployed to predict the heat of formation of 2,4-dichlorophenol.

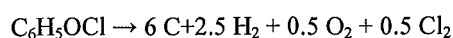
Table 2: The experimental standard molar enthalpy of formation in gas-phase for the compounds needed to form the isodesmic reactions [9].

Molecule	The standard molar enthalpy of formation (kJ/mol)
Benzene	82.6 ± 0.7
Phenol	-96.4 ± 0.9
Chlorobenzene	52.0 ± 1.3
1,2-Dichlorobenzene	30.2 ± 2.1
1,3-Dichlorobenzene	25.7 ± 2.1
1,4-Dichlorobenzene	22.5 ± 1.5
1,2,3-Trichlorobenzene	3.8 ± 0.7
1,2,4-Trichlorobenzene	-8.1 ± 1.0
1,3,5-Trichlorobenzene	-13.4 ± 1.0
1,2,3,4-Tetrachlorobenzene	-25.4 ± 1.0
1,2,3,5-Tetrachlorobenzene	-34.9 ± 1.0
1,2,4,5-Tetrachlorobenzene	-32.6 ± 0.8
Pentachlorobenzene	-40.0 ± 8.7

Table 4 compares the results from this study (CBS-QB3 and G4-MP2) with the results of Wang et al (G3X and G3X-MP2) [8] and with the experimental estimates from da Silva et al. for some monochlorophenols and dichlorophenols [4].

The predicted heats of formation are generally consistent with the available data in the literature. However, some notable differences can be highlighted between the experimental data obtained by da Silva et al and theoretically calculated heats of formation, which differ by up to 9 kJ/mol in the case of 3-chlorophenol. These experimental data were recently criticised by S. P. Verevkin et al for the simplified extrapolation procedure adopted by the group, [10] which suggest the difference between experimental measurements and simulation may be the result of experimental deficiencies.

We predict the entropy of formation and the Gibbs free energy of formation for all chlorophenols, using the heats of formation calculated by CBS-QB3, along with the entropy estimated by the same method. Initially, the entropy of formation was calculated based on the following chemical equation:



$$\Delta_f S_{298}^0 = S_{298}^0(2\text{-chlorophenol}) - 6 S_{298}^0(C(\text{graphite})) - 2.5 S_{298}^0(H_2(g)) - 0.5 S_{298}^0(O_2(g)) - 0.5 S_{298}^0(Cl_2(g))$$

Cl<sub>2</sub> (g) 223.08  
H<sub>2</sub> (g) 120.68

Table 4: Heats of formation and Gibbs free energy of formation calculated of chlorophenols (kJ/mol).

Method used	Standard heat of formation (gas-phase)					Standard Gibbs free energy of formation (gas-phase)	
	G4-MP2 <sup>a</sup>	CBS-QB3 <sup>a</sup>	G3X <sup>b</sup>	G3X-MP2 <sup>b</sup>	Exp. <sup>c</sup>	CBS-QB3 <sup>a</sup>	
Chlorophenol	2	-132.18	-132.97	-132.8	-132.8	-63.09	
	3	-126.11	-126.51	-126.2	-137	-137.0 ± 8.6	-57.42
	4	-123.99	-124.65	-124.2	-128.2	-128.2 ± 8.6	-55.64
	5	-126.09	-126.19	-126.1	-126.1		-57.07
	6	-119.06	-119.95	-119.5	-119.5		-50.70
Dichlorophenol	2,3	-154.09	-154.39	-154.5	-151.6	-151.6 ± 2.5	-79.28
	2,4	-155.89	-157.06	-156.6	-156.3	-156.3 ± 1.9	-82.48
	2,5	-153.49	-153.85	-161.9	-158.4	-158.4 ± 2.4	-79.20
	2,6	-151.25	-152.84	-152.5	-146.3	-146.3 ± 1.5	-77.89
	3,4	-145.52	-145.59	-145.7	-150.3	-150.3 ± 2.5	-71.42
	3,5	-151.29	-151.57	-151.8	-151.5	-150.3 ± 2.5	-77.64
	3,6	-140.47	-140.96	-149.1	-148.7		-66.93
	4,5	-145.35	-145.35	-145.6	-145.4		-71.18
	4,6	-142.70	-144.17	-143.4	-143.5		-70.17
5,6	-140.59	-140.75	-141.1	-140.9		-66.18	
Trichlorophenol	2,3,4		-179.36	-174.8	-174.7		-99.04
	2,3,5		-192.24	-179.6	-179.3		-112.31
	2,3,6		-186.90	-173.9	-173.7		-106.70
	2,4,5		-190.33	-177.3	-177.1		-110.56
	2,4,6		-190.28	-180.5	-179.7		-110.58
	2,5,6		-186.50	-	-		-106.29
	3,4,5		-171.61	-167.2	-166.9		-92.16
	3,4,6		-177.88	-164.6	-165.2		-98.74
	3,5,6		-178.84	-166.1	-165.7		-99.40
4,5,6		-165.72	-161.2	-161		-84.75	
Tetrachlorophenol	2,3,4,5		-207.45	-191.7	-190.4		-121.88
	2,3,4,6		-212.60	-192.4	-191.2		-127.21
	2,3,5,6		-210.95	-193.8	-192.4		-125.45
	2,4,5,6		-211.80	-191.6	-190.4		-126.40
	3,4,5,6		-194.16	-178.5	-177.1		-109.15
Pentachlorophenol		-216.95	-202.5	-201.9		-125.69	

a: estimated in this work, b: Wang et al. [8], c: da Silva et al. [4]

Table 3 lists the entropies of pure species necessary for the calculation of the entropies of formation of all chlorophenols.

Table 3: Standard entropies of elements used in the calculation of entropy of formation of chlorophenols [11].

Element	Entropy (J/mol·K)
C (graphite)	5.6
O <sub>2</sub> (g)	205.15

Using the equation:

$$\Delta_f G_{298}^0 = \Delta_f H_{298}^0 - T \Delta_f S_{298}^0$$

Table 4 lists the estimated Gibbs free energies of formation at 298.15 K for the chlorophenols.