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Experimental measurements and a group additivity approach for estimating the standard molar enthalpies of formation of dioxins

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The enthalpies of formation of dibenzo-*p*-dioxin and its polychlorinated derivatives have been measured, and a complete set of the enthalpies of formation has been constructed.

Understanding the reasons of the unusual stability of polychlorinated dibenzo-*p*-dioxins (PCDDs) is of primary importance. These reasons can be of kinetic or thermodynamic origin. In any case, reliable thermodynamic data are needed for the thermodynamic modelling of their formation. Meanwhile, the most important thermodynamic data, the standard molar enthalpies of formation ($\Delta_f H^0_m$), have never been measured experimentally; there are only some estimates of these values. In particular, the $\Delta_f H^0_m$ values of all 75 PCDDs were estimated by Shaub.[1] Recent re-estimations[2,3] of these values differ considerably from the Shaub's result. There is no doubt that all estimates will be more accurate, if reliable experimental values of $\Delta_f H^0_m$ for several model compounds will be available.

The aim of this work is to obtain experimentally the reliable values of $\Delta_f H^0_m$ for some PCDDs and based on these data to construct a complete set of enthalpies of formation of PCDDs.

Unsubstituted dibenzo-*p*-dioxin **1**, 1-chlorodibenzo-*p*-dioxin **2**, 2-chlorodibenzo-*p*-dioxin **3** and 2,3-dichlorodibenzo-*p*-dioxin **4** have been prepared by a standard procedure.[4] The substances were purified by recrystallization from ethanol or *o*-xylene and subsequently by vacuum distillation. The purity of the samples was determined using a Mettler differential scanning calorimeter (DSC-30). The melting temperatures, T_{fus}, and molar enthalpies of fusion, $\Delta_{fus} H^0_m$, were also measured (Table 1).

Table 1 Temperature and enthalpy of fusion and purity of the compounds.

Compound	T_{fus}/K	$\Delta_{fus} H^0_m$/kJ mol^{-1}	Purity, mole fraction
1	392.45±0.10	21.9±0.6	0.9990
2	373.95±0.14	20.0±1.1	0.9976
3	360.75±0.10	22.1±0.4	0.9975
4	431.60±0.20	27.1±0.6	0.9996

A rotating-bomb calorimeter,[5] was used in the combustion experiments. The platinum-lined bomb of volume 0.120 dm^3 was fitted with a tantalum lid. The temperature rise was measured with a copper resistance thermometer and a bridge circuit. The sensitivity of the temperature measurements was $\approx 5\times10^{-5}$ K. The products of combustion were analysed after each run according to a procedure described in ref. 6.

The enthalpies of sublimation were measured on a Calvet microcalorimeter using a standard procedure.[6]

The results and the derived thermochemical quantities (at T = 298.15 K) are presented in Table 2.

The derived values of $\Delta_f H^0_m$ (g) differ considerably from those estimated by Shaub[1] but they are close to recent estimates.[2]

The $\Delta_f H^0_m$ (g) values given in Table 2 indicate that the displacement of two hydrogen atoms in the 2- and 3-positions by chlorine atoms causes a difference in $\Delta_f H^0_m$ (g) values equal to -52.7 kJ mol^{-1}. The analogous difference between the $\Delta_f H^0_m$ (g) values of *o*-dichlorobenzene and benzene is equal to -52.4 kJ mol^{-1}. Almost the same heat effects of chlorination can be deduced from the enthalpies of formation of 2,3- and 3,4-dichlorophenols (-55.2 kJ mol^{-1} and -53.9 kJ mol^{-1} respectively[7]). For **2**, the effect of chlorination on the enthalpy of formation is equal to -29.0 kJ mol^{-1}. This value is also very close to that in monochlorobenzene (-30.6 kJ mol^{-1}). Obviously, the energetic effect of oxygen–chlorine interactions in PCDDs is not large, contrary to Shaub's estimation.[1] The $\Delta_f H^0_m$ (g) value of **3** represents the only exception to the general rule. To all appearances, a redeterminaton of this value is needed. This attempt was made recently with a sample of **3** (0.8 g, 0.9985 purity). Unfortunately, because the amount of the substance was small, we failed to determine accurately the combustion energy. However, the $-\Delta_c U^0_m$ (cr) value for **3** obtained in the preliminary experiments was about 12–15 kJ mol^{-1} lower than the value given in Table 2 in brackets, and thus the $-\Delta_f H^0_m$ (g) value was about 12–15 kJ mol^{-1} higher. In this situation, only the $\Delta_f H^0_m$ (g) values for **1**, **2** and **4** can be considered as a basis for estimating the $\Delta_f H^0_m$ (g) values of PCDDs.

To estimate the enthalpies of formation of all PCDDs, we used the difference method,[8,9] which is completely consistent with group additivity. Because the available experimental data on PCDDs are insufficient to develop an additive scheme for the prediction of enthalpies of formation of PCDDs, chlorinated benzenes were considered in this work as model compounds. This is in agreement with the above experimental results on the effect of chlorination. The enthalpies of formation were estimated on the assumption that the difference between these values for anyone of PCDDs and dibenzo-*p*-dioxin (DD) is equal to the difference between appropriate chlorinated benzene(s) and benzene. The chlorination of each ring in PCDDs is considered to have no influence on the other benzene ring. The enthalpies of formation for model compounds were obtained in this work for DD and taken from refs. 10 and 11 for benzene and chlorinated benzenes. An example is shown in Figure 1.

The same result can be obtained using group contribution values from Table 3. According to designation by Benson,[12] groups A and B can be written as C_B–(H) and C_B–(Cl),

Table 2 Experimental results and calculated values (kJ mol^{-1}).

Compound	$-\Delta_c U^0_m$ (cr)	$-\Delta_c H^0_m$ (cr)	$-\Delta_f H^0_m$ (cr)	$\Delta_{sub} H^0_m$	$-\Delta_f H^0_m$ (g)		
					this work	Ref. 1	Ref. 2
1	5714.2±4.1	5716.7±4.1	148.7±4.4	89.55±0.72	59.2±4.4	62.8	55.0
2	5561.5±4.4	5562.7±4.4	183.4±4.7	95.20±1.10	88.2±4.8	95.0	84.5
3	(5573.6±2.8)[a]	(5574.8±2.8)[a]	(171.3±3.2)[a]	97.24±0.55	(74.1±3.3)[a]	137.7	84.5
4	5406.4±6.6	5406.4±6.6	220.5±6.8	108.60±1.00	111.9±6.9	204.0	106.5

[a] Preliminary results. A new determination of this value is needed.

Table 3 Group additivity values for estimating the enthalpies of formation of PCDDs.

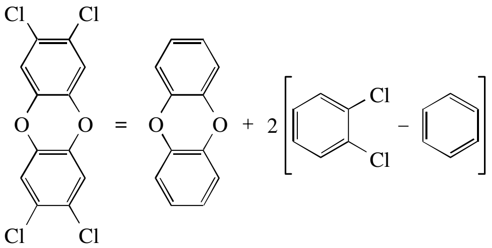
Group	Value/kJ mol^{-1}
A	13.765
B	–16.835
D	–16 9.32
$_{12}$	8.8
$_{13}$	4.3
$_{14}$	1.1
$_{123}$	13.0
$_{124}$	1.1
$_{1234}$	14.4

respectively. The group D consists of two O–$(C_B)_2$ and four C_B–$(C_B)_2(O)$ groups and describes the dioxin frame as a whole. Six corrections are used for 1,2-, 1,3-, 1,4-, 1,2,3-, 1,2,4- and 1,2,3,4-interactions of chlorine atoms. For example,

$$_{\mathrm{f}}H^0_{\mathrm{m}}\ (2,3,7,8\text{-TCDD}) = \mathrm{D} + 4\mathrm{A} + 4\mathrm{B} + 2\ _{12} = -164.0\ \mathrm{kJ\ mol^{-1}}$$

We estimate the error in the enthalpies of formation, calculated from the group increments, to be 10–40 kJ mol^{-1} depending on the chlorine content.

To estimate the gas-phase enthalpies of formation of PCDDs, Thompson[2] has developed a group contribution method based on the experimental data for chlorinated benzenes, quinones, hydroquinones and phenols. Pointing to the experimental errors in enthalpies of formation of chlorinated organic compounds, which are often considerable, Thompson[2] has excluded the experimental data by Platonov and Simulin[11] from consideration. At the same time, Thompson[2] has included the $_{\mathrm{f}}H^0$ (298.15 K) value for hexachlorobenzene, which was recommended by Pedley[10] although this value seems to be overestimated. Here, we prefered to base on the work,[11] which was made using carefully purified materials and properly tested methods. Different attitudes to the experimental data[11] are the main reason for discrepancies (up to 40 kJ mol^{-1}) in the enthalpies of formation estimated for PCDDs with high degrees of chlorination in this work and by Thompson.[2] We believe that, to remove the contradictions between these two models, reliable experimental data should be obtained for chlorinated benzenes and chlorinated dibenzo-*p*-dioxins with three or more chlorine atoms.



$_{\mathrm{f}}H^0$ −164.0 ⟵ −59.2 + 2 [30.2 − 82.6]

Figure 1 The derivation of the enthalpy of formation (kJ mol^{-1}) of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD).

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