ELSEVIER

Thermochimica Acta 261 (1995) 7–20

thermochimica acta

Enthalpies of formation and entropies of chlorinated dibenzo-*p*-dioxins and dibenzofurans; selected data for computer-based studies

D. Thompson

Department of Engineering Materials, University of Sheffield, Sheffield, S1 4DU, UK

Received 11 November 1994; accepted 27 February 1995

Abstract

Values for calculating the enthalpies of formation and standard entropies of chlorinated dibenzo-*p*-dioxins and dibenzofurans are obtained. The enthalpy of formation for dibenzo-*p*-dioxin derived from values for related compounds is -55 kJ mol^{-1}. The value of $\Delta_f H$ for dibenzofuran obtained by Chirico et al., 55.2 kJ mol^{-1}, is recommended. Basic reductions in the enthalpy of formation of 29.5 kJ mol^{-1} for each chlorine substitution, with positive corrections of 7.5 kJ mol^{-1} for each ortho- and 2.5 kJ mol^{-1} for each para-substitution, are derived from the enthaplies of formation of chlorinated benzenes. It is noted that a recent evaluation of the enthalpies of formation and sublimation of the mono- and dichlorophenols indicates that the enthalpies of formation of these and possibly other chlorinated aromatic compounds vary more regularly with degree of chlorination than previously thought, and the model of chlorination based on phenols due to Shaub is thus, in general, unsatisfactory. A previous model of dibenzo-*p*-dioxin and dibenzofuran chlorination based on benzoquinone chlorination due to the author may underestimate the reduction in enthalpy of formation for the higher degrees of chlorination. The values 388 J mol^{-1} K^{-1} (Shaub) and 374.4 J mol^{-1} K^{-1} (Chirico et al.) for the standard entropies of dibenzo-*p*-dioxin and dibenzofuran are recommended, with each chlorination increasing the entropy by 22.6 J mol^{-1} K^{-1}.

Keywords: Computer; Dibenzo-dioxin; Dibenzofuran; Enthalpy; Entropy

1. Introduction

The significance of dibenzo-*p*-dioxin and dibenzofuran and their chlorinated derivatives as environmental pollutants has led to attempts to derive thermodynamic data for them and to use such data to examine their general stability, conditions of formation,

SSDI 0040-6031(95)02310-0

relative abundance of isomers and homologues, and equilibrium concentrations relative to mixtures of other species. These efforts to derive data include a method of prediction of the enthalpy of formation of the chlorinated species using chlorination of phenol as the basis of adjustment of the enthalpy of formation for successive degrees of chlorination, due to Shaub [1]. A detailed examination of the entropy of dioxin and some chlorinated dioxins based on adjustment of vibrational frequencies, moments of inertia, etc., of benzene and chlorinated benzenes, and anthracenes, was carried out by the same author [2]. Spencer and Neuschutz [3] extended Shaub's data to condensed 2,3,7,8-tetrachlorodioxin by combining the gas phase result with data presented by Rordorf [4], and Schroy et al. [5] and examined its stability in the presence of varied concentrations of oxygen and chlorine. An investigation of relative concentrations of chlorinated dioxins and dibenzofurans by Thompson [6, 7], in which the enthalpies of formation are derived with reference to the differences in published enthalpies of formation of benzoquinone and its chlorinated derivatives, has been presented recently. He shows that his method and that of Shaub lead to prediction of radically differing isomer distributions whilst the Benson group additivity method using generalised parameters [8] gives a less varied distribution than either. Unsworth and Dorans [9] derived thermodynamic data for the species by the totally different approach of use of the MOPAC molecular structure predictive program [10]. Their results differ from those of Thompson in detail but there is general agreement in the range of isomer abundances for any particular degree of chlorination. This contrasts with predictions on the basis of Shaub's enthalpies of formation, which lead to a very wide range of relative abundances.

The present paper combines the outcome of the survey of thermodynamic data carried out in connection with the work reported in Refs. [6] and [7] with a revised summary of available experimental organic thermodynamic data due to Pedley [11], in order to provide a definitive basis for the derivation of enthalpies of formation and standard entropies of chlorinated dioxins and furans. The areas where further experimental information are most required are identified.

2. Assessments of enthalpies of formation

Three separate evaluations are required for the enthalpies of formation, i.e. those for (i) the enthalpy of formation of dibenzo-*p*-dioxin, (ii) the enthalpy of formation of dibenzofuran, and (iii) the effect on the enthalpy of formation of successive stages and positions of chlorination.

2.1. *Enthalpy of formation of dibenzo-*p*-dioxin*

No experimental determination of the enthalpy of formation of dioxin or any of its chlorinated derivatives is available. Shaub [1] used the conversion of 9,10-dihydroxyanthracene to dibenzopyran as the basis of an evaluation, with the second oxygen substitution altering the enthalpy of formation by the same amount as the first. Group additivity based on modification of two benzene molecules can also be used to obtain an enthalpy of formation, or an attempt can be made to derive data on the basis of trends in the enthalpies of formation of similar molecules. The experimental data is in fact sufficiently complete for substitutions between cyclohexane and dibenzo-*p*-dioxin for the procedure to be validated by application in extended form, as in Fig. 1. The processes of oxygen substitution of cyclohexane to dioxin (top row), addition of one benzene ring to each compound in the top row (second row) and addition of a second benzene ring (third row) produce trends which should allow an evaluation for dibenzo-*p*-dioxin at the lower right. The enthalpies of formation shown in Fig. 1 are taken from Ref. [11]. The specific sources are given in detail in Ref. [11] and are all established values and have not been changed for many years. It may be seen that the changes in the enthalpies of formation given between each pair are generally similar.

The NIST computer database [12] was also examined for any more recent information which may have been missed inadvertently, but there were no discrepancies except in the values given for 3,4-dihydro-2H-1-benzopyran, and 9,10-dihydroanthracene, which disagree with the values given in Ref. [11] by approximately 10 and 16 kJ mol^{-1} respectively. However, these are in fact estimates and not fundamental data.

Three of the substitutions shown in Fig. 1 follow the commonly observed trend for the change in enthalpy of formation resulting from the second substitution being smaller than that for the first substitution. This occurs on going from cyclohexane to dioxin, from cyclohexane to 9,10-dihydroanthracene, and from tetrahydro-2H-pyran to dibenzopyran. However, the changes in enthalpy of formation going to 2,3-dihydro-1,4-benzodioxin from both 1,4-dioxane and 3,4-dihydro-2H-1-benzopyran are respectively smaller and larger than expected if the normal trend were to be followed. The enthalpy of formation of 2,3-dihydro-1,4-benzodioxin is, therefore, regarded as suspect, and would merit re-evaluation. If the trends are followed, a true enthalpy of formation of approximately -182 kJ mol^{-1} for this substance is indicated by both horizontal and vertical conversions.

If the modified value for the enthalpy of formation of 3,4-dihydro-2H-1-benzopyran is adopted, the predicted enthalpy of formation of dibenzo-*p*-dioxin is 55 kJ mol^{-1}, which is reasonably close to the figure of 63 kJ mol^{-1} derived by Shaub.

2.2. *Enthalpy of formation of dibenzofuran*

A comparable exercise to that for dibenzo-*p*-dioxin to obtain the enthalpy of formation of dibenzofuran is, in principle, possible, starting with either furan or tetrahydrofuran. However, the data for the substances involved in either process is incomplete. Fortuitously, dibenzofuran has been the subject of a rigorous thermodynamic study by Chirico et al. [13]. Their result is $\Delta_f H = 55.22$ kJ mol^{-1}. Chirico et al. note that their result agrees with another recent result [14]. They also note that the difference between their enthalpy of combustion and the value obtained by Cass et al. [15] is only 0.5%, but that this is sufficient to lead to the significant discrepancy between their value for the enthalpy of formation and the previously accepted value (that of Cass et al. [15]), 83.3 kJ mol^{-1}.

The limitations of the data available for derivation of the enthalpy of formation of dibenzofuran by the same method as used for dibenzodioxin above, and the case made

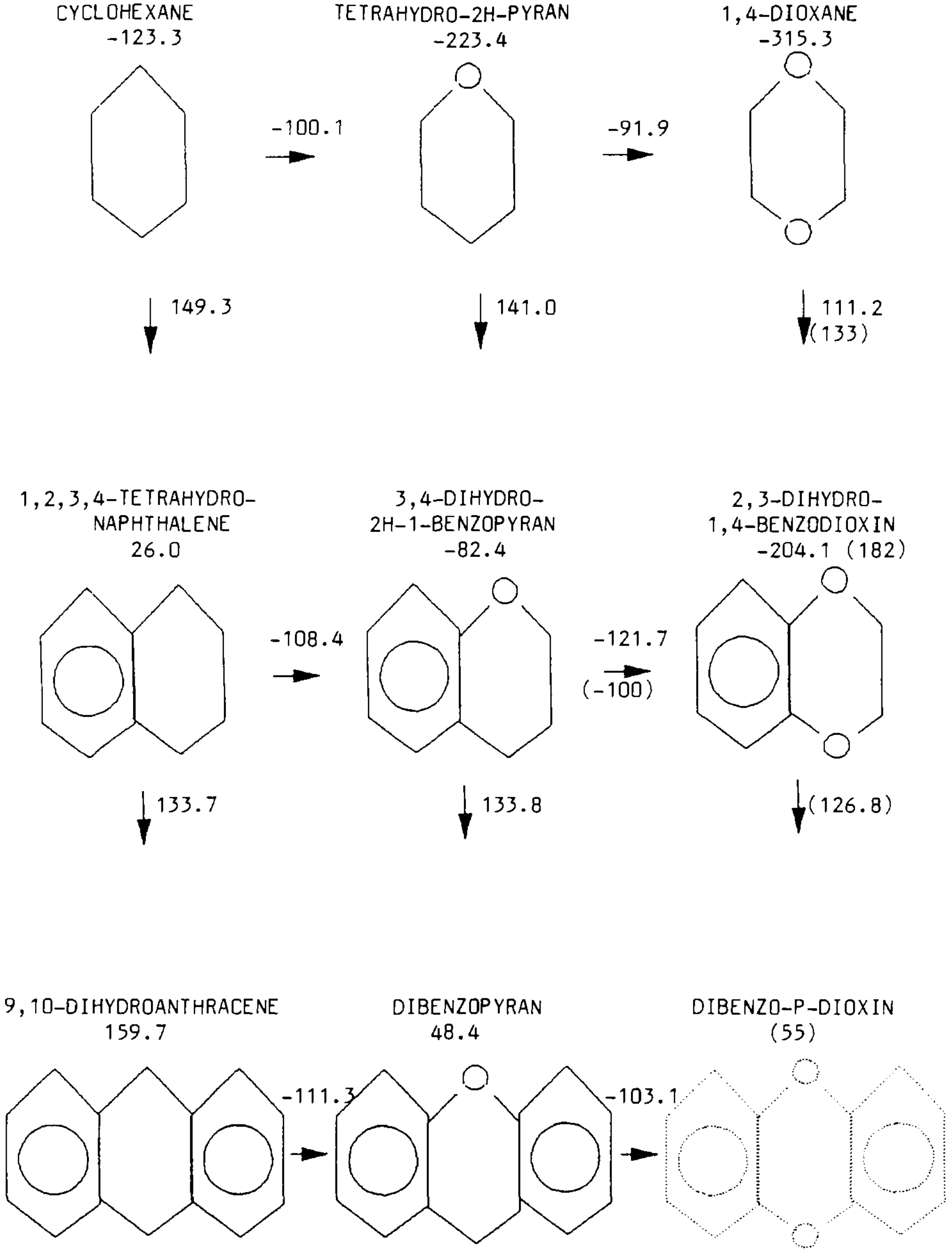

Fig. 1. Derivation of enthalpy of formation of dibenzo-*p*-dioxin: enthalpies of formation and changes in enthalpy between related compounds (kJ mol^{-1}).

by Chirico et al. for the consistency of their experimental value with another recent experimental value, lead to the recommendation of that value. The derivation exercise is therefore omitted.

2.3. *Effect of chlorination on enthalpy of formation*

In the case of dibenzo-*p*-dioxin, the chlorination of each of the rings can be considered to have no influence on the properties of the other benzene ring. This is less certain for dibenzofuran, but is regarded as a reasonable first approximation. Although it is possible that allowance for interaction associated with 1,9-substitution should be made, no definite value can be ascribed, and it is in any case expected to be small. There is no indication of strong oxygen–chlorine atom interactions in the literature.

Experimental enthalpies of formation for chlorinated organic compounds are often subjected to considerable uncertainties. This arises because the chlorine is not completely converted to hydrogen chloride in basic bomb calorimetry, and the preferred modification to procedure is use of a rotating bomb with arsenious acid added to reduce the chlorine. This increases the demands on experimental techniques, so that some caution must be exercised in accepting the data of any particular group. The situation is further complicated because it would appear that the effect of other functional groups on the change in enthalpy of formation due to chlorination is complex, and the effect also differs between aliphatic and aromatic compounds (see Ref. [11]). Because of the dependence on the type of compound chlorinated, examples used to assign values to the effect of chlorination on the enthalpy of formation of dioxins and dibenzofurans are confined to a few aromatic compounds and their chlorinated derivatives.

The direct effect of chlorination may be examined with reference to data on benzene and its chlorinated derivatives. The 'classical' literature contains values for benzene, chlorobenzene, the *o*-, *m*- and *p*-dichlorobenzenes, and hexachlorobenzene, and the assessed data are summarised in Table 1(a). There are additional results due to Platonov and Simulin [16] available for the stages of chlorination between the dichlorobenzenes and hexachlorobenzene. Insufficient details of this work are given to justify reliance on their values for accurate information.

Table 1
(a) Enthalpies of formation (kJ mol^{-1}) of condensed and gaseous benzene and mono-, di- and hexachlorobenzenes from Ref. [11]

Species	H_f for condensed	H_f for gas
Benzene	49.0	82.6
Monochlorobenzene	11.1	52.0
o-Dichlorobenzene	−17.5	30.2
m-Dichlorobenzene	−20.7	25.7
p-Dichlorobenzene	−42.3	22.5
Hexachlorobenzene	−127.6	−35.5

Shaub [1] attempted to extend the data to chlorination of a benzene ring with an oxygen atom attached by reference to benzene and phenol chlorination. The standard compilations note phenol, *m*- and *p*-chlorophenol, and pentachlorophenol enthalpies of formation only (Table 1(b)). The standard sources also include data for benzoquinone, benzoquinol, and their derivatives, obtained by Smith et al. [19]. These data are summarised in Table 1(c), together with the more recent results for dichlorophenols of da Silva et al. [18]. It is worth remarking on the quality of the work of Smith et al. [19], which covers a large number of chlorinated compounds. These data fall into three parts: a limited number of experiments carried out using a rotating bomb calorimeter; a large number using a static calorimeter; and some experiments carried out in the static calorimeter with the sample covered with cellophane. The rotating bomb calorimeter results were used as reference, and it was found that the result for *o*-dichlorobenzene was 2 kJ lower when burnt in an ampoule in the static bomb, and 5.8 kJ lower when covered with cellophane. The results obtained in the static bomb are therefore regarded as likely to be less than the true value for a given compound. Nonetheless, they are reasonably reliable inasmuch as the application of the technique and attention to experimental detail are fully reported and clearly conscientious. The results for samples covered with cellophane are commonly ignored since the potential error is serious.

The data in Table 2(c) have in common the combustion of the solid compound as the source of heats of combustion. They thus require the enthalpy of sublimation at

Table 1

(b) Enthalpies of formation (kJ mol^{-1}) of gaseous and condensed phenol, and mono-, di- and pentachlorophenols, and their enthalpies of sublimation

Species	H_f for condensed	H_f for gas	H_{sub}
Phenol	-165.1^a	-95.4^a	68.6^c
3-Chlorophenol	-189.3(liq)^a		
	-206.7^c	$-153.3^{a,c}$	53.1^c
			69.4^b
4-Chlorophenol	-181.3(liq)^a		
	-197.9^c	$-145.8^{a,c}$	51.9^c
			69.5^b
2,3-Dichlorophenol	-223.3^b	-151.6^b	71.7^b
2,4-Dichlorophenol	-226.4^b	-156.3^b	70.1^b
2,5-Dichlorophenol	-232.7^b	-158.4^b	73.6^b
2,6-Dichlorophenol	-222.1^b	-146.3^b	75.8^b
3,4-Dichlorophenol	-231.6^b	-150.3^b	81.3^b
3,5-Dichlorophenol	-231.8^b	-148.2^b	82.8^b
Pentachlorophenol	-292.5^a	-225.1^a	67.4^c

[a] From Ref. [11]. These and the corresponding values in Ref. [17] differ only slightly: no adjustment to heats of sublimation has been made to conform with the small differences.

[b] From Ref. [18].

[c] From Ref. [17].

Table 1
(c) Enthalpies of formation (Ref. [11]) and enthalpies of sublimation (Ref. [20]) (kJ mol^{-1}) of benzoquinone and hydroquinone and their chlorinated derivatives

Species	H_f for condensed	H_f for gas	H_{sub}
Benzoquinone	−185.7	−122.9	62.8
2-Chlorobenzoquinone	−220.6	−151.6	69.0
2,3-Dichlorobenzoquinone	−248.1		
2,5-Dichlorobenzoquinone	−245.2		
2,6-Dichlorobenzoquinone	−244.3	−174.5	69.9
Trichlorobenzoquinone	−269.5	−185.7	98.7
Hydroquinone	−364.5	−265.3	99.2
2-Chlorohydroquinone	−382.8	−314.0	69.0
2,3-Dichlorohydroquinone	−416.3		
2,5-Dichlorohydroquinone	−427.3		
2,6-Dichlorohydroquinone	−423.5	−331.5	92.0
Trichlorohydroquinone	−440.7	−339.4	101.3
Tetrachlorohydroquinone	−453.6		

298.15 K for their conversion to enthalpy of formation of the gas. From the table it may be seen that there is a trend for the heats of combustion of the solid compounds to decrease with increasing degree of chlorination, except on going from hydroquinone through chloroquinone to the dichloroquinones. The overall change in enthalpy of formation on going from hydroquinone to the dichlorohydroquinones is of the same order (60 kJ mol^{-1}) as two chlorinations derived from benzene chlorination, however, so that the high difference in the enthalpies of formation of benzoquinone and chlorobenzoquinone, and the small difference in the enthalpies of formation for chloroquinone and the dichloroquinones, are either due to an unusual lack of stability of chlorohydroquinone, or an error in the measurement (which is attributed with an error of ± 8.4 kJ mol^{-1} by Cox and Pilcher [17]).

The conversion of this data for the solid to gas phase enthalpies of formation using the earlier data for enthalpies of sublimation leads to some additional anomalies. The possibility that at least some of the apparently erratic effects of chlorination on the heat of combustion may be due to inaccurate data for enthalpies of sublimation is highlighted by the data of da Silva et al. [18] for chlorophenols. If their enthalpies of sublimation are combined with the currently accepted enthalpies of formation of the solid phase [17], and the resulting gas phase enthalpies of formation are compared with the gas phase enthalpies of formation of phenol and the dichlorophenols, it is seen that the effect of chlorination is broadly in agreement with the model of 30 kJ mol^{-1} for each chlorination, with some adjustment for interactions. It seems possible that the observed strongly decreasing change in enthalpy of formation with degree of chlorination in the benzoquinone series is due to increasingly high values for the enthalpy of sublimation, and re-measurement of this value would be desirable. (The possibility that there are errors in the enthalpies of formation remains, of course, and re-estimation of these values would also be desirable.)

Table 2
Isomer abundances for tri- and pentachlorodioxins and tetrachlorodibenzofurans predicted by the present work and by the method presented in Ref. [6]
(a) Abundances for tetrachlorodibenzofurans

Isomer	This work % ('Bz')	From Ref. [6] % ('Qn')	Bz/Qn
1234	0.086	$<10^{-4}$	
1236	0.592	0.025	23.68
1237	0.592	0.025	23.68
1238	0.592	0.025	106.56
1347	2.664	0.025	106.56
1348	2.664	0.025	106.56
2346	0.592	0.025	23.68
2348	0.592	0.025	23.68
2349	0.592	0.025	23.68
1246	2.477	0.073	33.93
1247	2.477	0.073	33.93
1248	2.477	0.073	33.93
1239	0.604	0.006	100.67
1349	2.718	0.006	453.00
1249	2.527	0.017	148.65
1267	0.978	0.693	1.41
3467	0.489	0.693	0.71
1268	2.477	3.590	0.69
1367	2.477	3.590	0.69
2467	2.477	3.590	0.69
1369	10.427	10.726	0.97
1468	10.427	10.726	0.97
1269	4.171	0.524	7.96
1289	0.997	0.177	5.63
1278	0.978	0.83	1.18
2367	0.978	0.83	1.18
1478	4.088	2.453	1.67
1279	2.527	0.722	3.50
1368	6.317	18.784	0.34
2468	3.159	18.784	0.17
1378	2.477	4.3	2.00
1469	8.781	6.363	1.38
2368	2.477	4.3	0.58
2378	0.489	0.994	0.49

In summary, the chlorination of benzene indicates that chlorine–chlorine interactions are strongest at the ortho position, weaker at the meta, and minimal at the para. The compounds chosen in a previous study [6, 7] as being nearest in structure to chlorinated dioxins, the substituted benzoquinones, reflect this in progressively less reduction in enthalpy of formation per chlorination with initial degree of substitution, but the effect is much stronger than for benzene. The hydroxy-group-containing series

Table 2
(b) Abundances for trichlorodibenzo-*p*-dioxins

Isomer	This work %('Bz')	From Ref. [6] %('Qn')	Bz/Qn
123	0.558	0.098	5.81
124	3.878	1.991	1.95
126	3.878	2.728	1.42
127	3.878	2.728	1.42
128	3.878	2.728	1.42
129	3.878	2.728	1.42
136	9.902	16.072	0.62
137	9.902	16.072	0.62
138	9.902	16.072	0.62
139	9.902	16.072	0.62
146	16.344	8.130	2.01
147	16.344	8.130	2.01
236	3.878	3.268	1.18
237	3.878	3.268	1.18

Table 2
(c) Abundances for pentachlorodibenzo-*p*-dioxins

Isomer	This work % ('Bz')	From Ref. [6] % ('Qn')	Bz/Qn
12346	0.905	0.046	19.64
12347	0.905	0.046	19.64
12367	1.494	1.671	0.89
12368	3.814	9.854	0.39
12369	6.295	4.984	1.26
12378	1.494	2.001	0.75
12379	3.814	9.854	0.39
12389	1.494	1.671	0.89
12467	6.295	4.984	1.26
12468	16.072	29.370	0.55
12469	26.528	14.857	1.79
12478	6.295	12.037	0.52
12479	18.301	3.302	5.54
12489	6.295	4.984	1.26

of phenols and hydroxyquinones show erratic behaviour, with the effect of chlorination varying within wide limits and showing little tendency towards a consistent decrease with degree of chlorination (if classical values for the enthalpy of sublimation are accepted). However, the use of recent values for the enthalpies of sublimation of monochlorodioxins brings the results for the phenol series much closer in behaviour to benzene chlorination. It is also of note in this connection that values for the enthalpies of sublimation of chlorinated dioxins obtained by Rordorf et al. [21] follow a steady trend of increasing enthalpy of sublimation with degree of substitution, in contrast to the erratic variation noted for the benzoquinone and hydroquinone series, which are of much earlier origin [20]. If wide error limits are accepted for earlier values of enthalpies of sublimation, and it is taken into account that the results of Smith et al. [19] for enthalpies of formation of the chlorinated species are somewhat low, these results are also consistent with the results for benzene.

It is therefore recommended that the value 29.5 kJ mol^{-1} is used for chlorine substitution in dibenzo-*p*-dioxins or dibenzofurans, with 7.5 kJ mol^{-1} correction applied for each ortho interaction, and 2.5 kJ mol^{-1} applied for each meta interaction.

3. Standard entropy

The standard entropy values are of significance in calculation of Gibbs free energies for equilibria involving substituted dibenzodioxins and dibenzofurans, and their importance increases with increasing temperature. They are dependent on three-centre interactions and consequently are less amenable to group additivity predictive methods than enthalpies of formation.

*3.1. Standard entropy of dibenzo-*p*-dioxin*

The Benson group additivity result for dibenzo-*p*-dioxin entropy is 296 J mol^{-1} K^{-1} from the values given in the CHETAH computer database (with the carbonyl group used to represent the C_B–O group [22]). The more recent values of Domalski and Hearing [23] for group contributions omit the value for entropy for the O–$(C_B)_2$ group, and therefore also require use of the value for a similar group. Shaub [2] used modification of the vibrational frequencies of anthracene on the basis of vibrational frequencies for the oxygen bridge of dibenzofuran to derive an entropy for dioxin of 388 J mol^{-1} K^{-1}. The discrepancy is large, and since the value obtained by Shaub does not incorporate a large change from that for the model compound (anthracene), and is similar to the experimental value for the closely related compound dibenzofuran (see below), it is regarded as a reasonable estimate.

3.2. Standard entropy of dibenzofuran

The standard entropy of dibenzofuran is reported as 374.4 J mol^{-1} K^{-1} by Chirico et al. [13]. The result reported in Ref. [7] (402.2 J mol^{-1} K^{-1}) represents an attempt to adjust from the group additivity result, for which the group corresponding to the direct link between the benzene rings is not available. The value obtained by Chirico et al. is regarded as reliable.

3.3. Effect on standard entropy of chlorination

The effect of chlorination on the standard entropy is given in group additivity tabulations [22] as 30.48 J mol^{-1} K^{-1}. This value was used in Refs. [6] and [7]. Shaub obtained standard entropies for some chlorinated dioxins (1-chloro-, 2-chloro-, 2,3,7,8-tetrachloro-, and octachlorodibenzo-*p*-dioxin), using chlorination of benzene as the model on the basis of which the dibenzo-*p*-dioxin frequencies could be modified. The total entropy change for the first four chlorinations (90.46 J $\mathrm{mol^{-1}\,K^{-1}}$) is sufficiently close to the entropy change for the last four chlorinations (94.01 J $\mathrm{mol^{-1}\,K^{-1}}$) to assume a mean value per chlorination of 22.6 J $\mathrm{mol^{-1}\,K^{-1}}$, with no interaction term included.

4. Comparison with previous results: equilibria between isomers and congener groups

The equilibrium isomer distributions predicted using the benzoquinone-based model [6] and the present model are shown for tri- and pentachlorodioxins, and tetrachlorofurans, at 600 K, in Table 2. The discrepancy between the two sets of predictions is not serious for the majority of the isomers, when the high sensitivity of equilibrium concentrations to enthalpies of formation is taken into account. In the case of a few isomers the difference is more marked; for instance, the benzoquinone-based model predicts destabilisation of 1,4,6,9-tetrachlorodibenzofuran because the model regards the effect of chlorination of each ring as equivalent to the effect of formation of dichlorobenzoquinone from benzoquinone, with attendant chlorine–chlorine interactions reducing the change in enthalpy of formation due to chlorination. However, the current model considers that there is no interaction between any of the substituents in this isomer.

Isomer group terms have been derived as described in Ref. [7]. The relative abundances of the isomer groups have been calculated using the 'MULTIPHASE' module of the NPL MTDATA predictive program, for a C:H:O:Cl ratio of 12:100:1.5:100, at temperatures of 300 and 600 K. The high levels of chlorine and hydrogen ensure that the ratios of the unchlorinated species and the various degrees of chlorination are virtually independent of the chlorine and hydrogen levels. Molecular chlorine and hydrogen are included in the predictive database to absorb the excess of these species. The results are given in Table 3. The ratio of the present predictions to that of the earlier database reflects the higher positive contribution to the enthalpy due to interactions between the substituents which is included in the earlier model. The current model predicts more bias towards formation of the more highly substituted species than does the earlier model.

5. Conclusions

1. The most likely value of the enthalpy of formation of dioxin is -55 kJ $\mathrm{mol^{-1}}$. This is derived by following trends in the value of substances obtained when substitutions are made in cyclohexane. A direct experimental determination would be needed for any further degree of confidence in the value. A value of 388 J $\mathrm{mol^{-1}\,K^{-1}}$ for the entropy, due to Shaub, is consistent with data for similar compounds.

Table 3

Logarithms of equilibrium constants for conversion of equilibrium isomer groups of chlorinated dioxins and dibenzofurans predicted by the method given in Ref. [6] to those predicted in the present work: values for pentachloro- groups C12H3Cl5O ⟨g⟩ (Ref. [6]) = C12H3Cl5O⟨g⟩(this work)

T/K	$-G/RT\ln 10$
298.15	1.964
300.00	1.937
400.00	0.921
500.00	0.350
600.00	−0.013
700.00	−0.264
800.00	−0.448
900.00	−0.589
1000.00	−0.700

C12H3Cl5O2⟨g⟩(Ref. [6]) = C12H3Cl5O2⟨g⟩(this work)

T/K	$-G/RT\ln 10$
298.15	6.003
300.00	5.986
400.0	5.349
500.00	5.032
600.00	4.850
700.00	4.735
800.00	4.657
900.00	4.599
1000.00	4.556

2. The recent experimental values, 55.2 kJ mol^{-1} for the enthalpy of formation of dibenzofuran, and 374.4 J mol^{-1} K^{-1} for the standard entropy, obtained by Chirico et al., are recommended.

3. Calculation of the effect of chlorination on the enthalpy of formation of the compound is recommended to involve a basic reduction in the enthalpy of formation by 29.5 kJ mol^{-1}, with the effect reduced by 7.5 kJ mol^{-1} for each ortho-relationship with another chlorine atom on the same ring which it introduces, and 2.5 kJ mol^{-1} for each meta-relationship it introduces. There is a need for more accurate values for polychlorinated benzenes if confidence in values for the more heavily chlorinated dibenzo-*p*-dioxins and dibenzofurans is to be established. The entropy change for each chlorination can be taken to be 22.6 J mol^{-1} K^{-1}.

Acknowledgements

The author is very grateful to Dr. J.B. Pedley for advice on selection of thermodynamic data and discussion of the extrapolation of data to related compounds. He is also grateful to Professor B.B. Argent for his advice and support. The research was funded under ECSC Agreement No. 7220-EC/861.

References

[1] W.M. Shaub, Procedure for estimating the heats of formation of aromatic hydrocarbons: chlorinated benzenes, phenols and dioxins, Thermochim. Acta, 55 (1982) 59–73.

[2] W.M. Shaub, Estimated thermodynamic functions for some chlorinated benzenes, phenols and dioxins, Thermochim. Acta, 58 (1982) 11–44.

[3] P.J. Spencer and D. Neuschutz, Thermodynamic conditions for the formation of dioxin, Chem. Eng. Technol., 15 (1992) 119–123.

[4] B.F. Rordorf, Thermal properties of dioxins, furans and related compounds, Chemosphere, 15 (1986) 1325–1332.

[5] J.M. Schroy, F.D. Hileman and S.C. Cheng, Physical/chemical properties of 2,3,7,8-TCDD, Chemosphere, 14 (1985) 877–880.

[6] D. Thompson, An evaluation of the heat of formation of chlorinated dioxins and its application to isomer abundance predictions, Chemosphere, 29 (1994) 2545–2554.

[7] D. Thompson, Thermodynamic considerations in dibenzodioxin and dibenzofuran formation, Chemosphere, 29 (1994) 2583–2595.

[8] S.W. Benson, Thermochemical Kinetics, 2nd edn., John Wiley, New York, 1976.

[9] J.F. Unsworth and H. Dorans, Thermodynamic data for dioxins from molecular modeling computations: predictions of equilibrium isomer composition, 12th International Symposium on Chlorinated Dioxins and Related Compounds, 24th–28th August, 1992, Tampere, Finland.

[10] J.J.P. Stewart, MOPAC: a semiempirical molecular orbital program, J. Computer Aided Design, 4 (1990) 1–105.

[11] J.B. Pedley, Thermochemical Data and Structures of Organic Compounds, Vol. 1, Thermodynamics Research Center, Texas, 1994.

[12] NIST Standard Reference Database 25, Version 1.2, Sept. 1991, National Institute of Standards and Technology, Gaithersburg, MD.

[13] R.D. Chirico, B.E. Gammon, S.E. Knipmeyer, A. Nguyen, M.M. Strube, C. Tsonopoulos and W.V. Steele, The thermodynamic properties of dibenzofuran, J. Chem. Thermodyn., 22 (1990) 1075–1096.

[14] R. Sabbah and I. Antipine, Thermodynamic studies on four polycycles. Relationship between their energy values and their structure, Bull. Soc. Chim. Fr., (1987) 392–400.

[15] R.C. Cass, S.E. Fletcher, C.T. Mortimer, H.D. Springall and T.R. White, Heats of combustion and molecular structure. Part V. The mean bond energy term for the C–O bond in ethers, and the structures of some cyclic ethers, J. Chem. Soc., (1958) 1406.

[16] V.A. Platonov and Yu. N. Simulin, Standard enthalpy of formation of 1,2,3-trichlorobenzene, 1,2,4,5-tetrachlorobenzene and hexachlorobenzene, Zh. Fiz. Chim., 57 (1983) 1387–1391; Experimental determination of the standard enthalpy of formation of polychlorobenzenes. II. Standard enthalpy of formation of dichlorobenzenes, Zh. Fiz. Chim., 58 (1984) 2682–2686; Experimental determination of the standard enthalpy of formation of polychlorobenzenes. III. Standard enthalpy of formation of mono, 1,2,4-, 1,3,5-tri, 1,2,3,4- and 1,2,3,5-tetrachlorobenzenes, Zh. Fiz. Chim., 59 (1985) 300–304.
V.A. Platonov, Yu.N. Simulin and M.M. Rosenberg, Standard enthalpy of formation of pentachlorobenzene. Calculation of ΔH_c(g) and ΔH_f(g) of polychlorobenzenes by the Tatevskii method, Zh. Fiz. Chim., 59 (1985) 1378–1383.

[17] J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London and New York, 1970.

[18] M.A.V. Ribiero da Silva, M.L.C.C.H. Ferrao and F. Jiye, Standard enthalpies of combustion of the six dichlorophenols by rotating-bomb calorimetry, J. Chem. Thermodyn., 26 (1994) 839–846.

[19] L. Smith, L. Bjellerup, S. Krook and H. Westermark, Heats of combustion of organic chloro compounds determined by the 'quartz wool' method, Acta Chim. Scand. 7 (1953) 65–86.

[20] A.S. Coolidge and M.S. Coolidge, The sublimation pressures of substituted quinones and hydroquinones, J. Am. Chem. Soc., 49 (1927) 100.

[21] B.F. Rordorf, L.P. Sarna, G.R.B. Webster, S.H. Safe, L.M. Safe, D. Lenoir, K.H. Schwind and O. Hutzinger, Vapour pressure measurements on halogenated dibenzo-*p*-dioxins and dibenzofurans. An extended data set for a correlation method, Chemosphere, 20 (1990) 1603–1609.

[22] C.A. Davies, E. Freedman, D.J. Frurip, G.R. Hertel, W.H. Seaston and D.N. Treweek, CHETAH, the ASTM chemical thermodynamic and energy release evaluation program (2nd edn.), Version 4.4, ASTM, 1990.

[23] E.S. Domalski and E.D. Hearing, Estimation of the thermodynamic properties of C–H–N–O–S–halogen compounds at 298.15 K, J. Phys. Chem. Ref. Data, 22 (1993) 805–1174.