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PROCEDURE FOR ESTIMATING THE HEATS OF FORMATION OF AROMATIC COMPOUNDS. PART II. CHLORINATED PHENOLS, BIPHENYLS, DIPHENYL ETHERS AND DIBENZOFURANS

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ABSTRACT

A previously developed group contribution method is used to estimate the gas phase enthalpies (heats) of formation of chlorinated phenols, diphenyl ethers and dibenzofurans. A slight extension of the method is used to estimate the gas phase enthalpies (heats) of formation of chlorinated biphenyls. In general, it is noted that the enthalpy of formation tends to be lower with increased degree of chlorination and with increased oxygen content in the molecules. Variations among isomers are attributable to nearest neighbor effects when using the method described herein. Limitations of the method are briefly discussed.

INTRODUCTION

A method has been described previously for estimating the gas phase enthalpies of formation of some chlorinated aromatic compounds [1], which was applied to chlorinated benzenes, dibenzo-*p*-dioxins and some phenols. The method has been shown to be simple and of practical utility, particularly in the absence of experimental thermodynamic data. As was noted previously [1], there is a marked absence of experimental thermodynamic data for chlorinated aromatic compounds. Many of these compounds are generally regarded to be hazardous and/or toxic in nature [2–4]. Therefore it is important to characterize their physical and chemical properties to the greatest possible extent.

There is considerable interest in the prospects for disposal via thermal incineration of these and other hazardous waste materials [2–7]. Chlorinated hazardous waste chemicals may prove to be among the most difficult to incinerate of those compounds commonly found in typical hazardous waste feedstocks [8,9]. In this respect, kinetic and thermodynamic data would be particularly useful. Therefore, as an extension of the previous work, an application of the estimation method to the calculation of the gas phase heats of formation of diphenyl ethers, dibenzofurans and some additional

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phenols is presented here. In addition, a slight extension of the previous method is applied for estimating the gas phase heats of formation of chlorinated biphenyls. This work is presented in response to a congressional mandate to the National Bureau of Standards under the direction of the Resource Conservation Recovery Act of 1976 (RCRA), Sect. 5002.

It is important to emphasize again that there is at present considerable uncertainty about the reliability of the thermodynamic data base for chlorinated organic compounds [1]. This will be discussed later in this paper. In light of these uncertainties, the reader is cautioned that the data in the tables in this paper and those in ref. 1 are to be regarded strictly as estimates, which are adequate for determining, in conjunction with additional entropy and heat capacity data, whether or not gas phase thermodynamic equilibrium controls in a limiting way the destruction of chlorinated organic compounds at elevated temperatures as in combustion processes, e.g. thermal incineration. These estimates should not be used for other types of processes for reasons discussed later.

METHODOLOGY

The method used to estimate the gas phase enthalpies of formation of chlorinated aromatic compounds is briefly outlined. For additional information, the reader is referred to a more detailed and explicit description of the procedure in a previous report [1]. In essence, the determination of the gas

TABLE 1

Summary of primary and secondary substituent interaction effects referred to Benzene as a starting compound

Effect	Correction [a] (kcal mole^{-1})	Remarks
χ	7.6 ±0.21	Chlorine substitution
β	42.85±0.25	OH substitution
o_{11}	2.1 ±0.5	Cl, Cl *ortho* interaction
m_{11}	1.0 ±0.6	Cl, Cl *meta*
p_{11}	0.4 ±0.4	Cl, Cl *para*
o_{12} (I)	2.0 ±3.6	Cl, OH *ortho* (OH adjacent to one Cl atom)
o_{12} (II)	6.4 ±5.0	(OH symmetrically surrounded by Cl)
m_{12}	−6.1 ±2.1	Cl, OH *meta*
p_{12}	−4.3 ±2.1	Cl, OH *para*
ξ	1.6 ±1.5	(2,6′), (2,2′), (6,2′), (6,6′) interactions

[a] Values of corrections taken from ref. 1, except ξ; the uncertainty limits are ± the square root of the sum of the squared uncertainties associated with the original literature values used to calculate the interaction effects.

phase heat of formation of a chlorine substituted aromatic compound requires that account is made (a) for the primary effect of replacing a hydrogen atom with a chlorine atom, and (b) the secondary effect of *ortho-*, *meta-* and *para*-substituent interactions between chlorine atoms or other substituent groups. By use of thermodynamic data reported for "model" compounds, numerical values for these effects as they relate to the gas phase heats of formation have been determined by the author. These effects are summarized in Table 1 of this paper. The uncertainty limits reported in Table 1 are calculated as ± the square root of the sum of the squared uncertainties associated with the original literature values reported for the heats of formation of compounds used in the calculation of the interaction effects [1]. Previously, some comparisons have been shown between estimated and experimentally reported values for the gas phase heats of formation of some methyl-, chloro- and fluoro-substituted benzene compounds to indicate the extent to which experimental data may be reproduced, as well as to suggest the likely error limits one might expect via this estimation scheme.

Experimental values for the gas phase heats of formation for diphenyl ether, biphenyl, phenol and dibenzofuran have been reported in the literature, as listed in Table 2. The calculation of the estimated gas phase heats of formation is illustrated for some typical chlorine substituted molecules from the above classes of compounds, using the data presented in Tables 1 and 2.

2,3,3′,4,4′-Pentachlorodiphenyl ether

$$\Delta H_f^0(298.15\ \text{K, g}) = DPE - 5\chi + 3o_{11} + m_{11} + o_{12}(\text{II}) + 2m_{12} + 2p_{12}$$
$$= -33 \pm 7\ \text{kcal mole}^{-1}$$

TABLE 2

Thermodynamic data for some organic compounds [10]

Compound	ΔH_f^0(298.15 K, g) (kcal mole^{-1})
Benzene	19.81 ± 0.13
Phenol	−23.04 ± 0.21
Biphenyl	43.53 ± 0.6
Diphenylether	11.94 ± 0.67
Dibenzofuran	19.9 ± 1.2
2,2′-Dichlorobiphenyl	30.5 ± 1.1
4,4′-Dichlorobiphenyl	28.9 ± 1.0
Dibenzo-*p*-dioxin	−15 ± 2 [a]

[a] ΔH_f^0 is estimated from ref. 1; the uncertainty is calculated as described in the footnote to Table 1 using the literature values [10] reported for the uncertainties in ΔH_f^0 for 9,10-dihydroanthracene and dibenzopyran.

DPE is the gas phase heat of formation of the unsubstituted diphenyl ether, taken from Table 2. The second term on the right-hand side of the equation above is the primary substituent correction. The remaining terms are the secondary interaction corrections.

2,3,6,7-Tetrachlorodibenzofuran

$$\Delta H_{\mathrm{f}}^{0}(298.15\ \mathrm{K,\ g}) = DBF - 4\chi + 2m_{12} + p_{12} + o_{12}(\mathrm{II}) + 2o_{11}$$
$$= -16 \pm 6\ \mathrm{kcal\ mole}^{-1}$$

DBF is the gas phase heat of formation of the unsubstituted dibenzofuran, taken from Table 2. The remaining terms on the right-hand side of the equation above are the primary substituent and secondary interaction effects, as noted previously.

2,3,5-Trichlorophenol

$$\Delta H_{\mathrm{f}}^{0}(298\ \mathrm{K,\ g}) = B - \beta - 3\chi + o_{12}(I) + 2m_{12} + o_{11} + m_{11} + p_{11}$$
$$= -52 \pm 5\ \mathrm{kcal\ mole}^{-1}$$

2,3,6-Trichlorophenol

$$\Delta H_{f}^{0}(298.15\ \mathrm{K,\ g}) = B - \beta - 3\chi + 2o_{12}(\mathrm{II}) + m_{12} + o_{11} + m_{11} + p_{11}$$
$$= -36 + 7\ \mathrm{kcal\ mole}^{-1}$$

B is the heat of formation of unsubstituted benzene, taken from Table 2. The additional terms on the right-hand side of the equations above are as described previously. Note that in the case of phenols, the hydroxyl group being adjacent to one Cl atom is distinguished from the hydroxyl group which is symmetrically surrounded by two Cl atoms. This distinction is utilized in calculating the gas phase heat of formation of phenols to differentiate between the latter case, where the competitive effect of two *ortho*-chlorine substituents is likely to raise the value of the gas phase heat of formation, and in the former case, where in the absence of a competitive effect, hydrogen bonding between the hydrogen atom of the OH group and the adjacent chlorine atom on the benzene ring may result in a lower estimated value of the gas phase heat of formation [1]. In the latter case, as in ref. 1, the $o_{12}(\mathrm{II})$ correction is used, and it is assumed as before, equivalent to the average *ortho* effect associated with the compounds pentachlorophenol, 1,4-dihydroxytrichlorobenzene and 1,4-dihydroxy-2,6-chlorobenzene. The $o_{12}(\mathrm{II})$ correction is used in estimating gas phase heats of formation for the diphenyl ethers and the dibenzofurans as was done previously for the dioxins [1], as there is no possibility of intramolecular hydrogen bonding.

The gas phase heats of formation for chlorinated biphenyls can be estimated from the data presented in Tables 1 and 2. One additional correction term, ξ, is utilized. This correction term accounts for the interaction effect associated with chlorine substitution in the 2 and 2′, 2 and 6′, 6 and 2′, or 6 and 6′ positions. These positional interactions are assumed to be equivalent. This interaction effect is taken as the difference between the values reported in the literature for the gas phase heats of formation of 2,2′-dichlorobiphenyl and 4,4′-dichlorobiphenyl [10]. Three examples of the calculation of gas phase heats of formation for chlorinated biphenyls are presented.

2,3,4,6,3′-Pentachlorobiphenyl

$\Delta H_f^0(298.15\text{ K, g}) = BP - 5\chi + 2o_{11} + 3m_{11} + p_{11} = 13 \pm 2\text{ kcal mole}^{-1}$

2,3,4,2′,5′-Pentachlorobiphenyl

$\Delta H_f^0(298.15\text{ K, g}) = BP - 5\chi + 2o_{11} + m_{11} + p_{11} + \xi = 13 \pm 2\text{ kcal mole}^{-1}$

2,3,4,6,2′-6′-Hexachlorobiphenyl

$\Delta H_f^0(298\text{ K, g}) = BP - 6\chi + 2o_{11} + 4m_{11} + p_{11} + 4\xi = 13 \pm 3\text{ kcal mole}^{-1}$

BP is the gas phase heat of formation of the unsubstituted biphenyl, taken from Table 2. The corrections for primary and secondary interaction effects are as noted previously. In addition, the use of the correction term, ξ, is illustrated.

DISCUSSION

Alkyl-substituted aromatic compounds have been treated in a more detailed version of this method in refs. 11 and 12 in which *ortho, meta, para* and buttress effects are considered. Because there are too few high quality data on polychlorinated aromatics [1], simplifications are desirable here. Notwithstanding this observation, as indicated, the estimated gas phase heats of formation are quite useful towards modeling the high temperature equilibrium thermodynamics of combustion processes such as thermal incineration [8,9]. This usefulness derives from the fact that in practical high temperature combustion, the principal driving force which describes the equilibrium thermodynamics for large organic molecules such as those described here is primarily defined by the stoichiometric coefficient associated with carbon dioxide formation. Thus, substantial uncertainties are tolerable in the estimates of the heats of formation of these molecules for this application. However, there is a need for caution in the use of these estimates for other purposes, e.g. the determination of equilibrium isomeric product distributions at ambient temperatures.

This is because the determination of the distribution of isomeric products depends upon the small differences between heats of formation of isomers. The data used here for calculating heats of combustion are not accurate enough to determine these small differences. The difference (as determined from Table 3) in the heats of formation for 2,5- and 2,6-dichlorophenol, 17

TABLE 3

Gas phase heats of formation for polychlorinated phenols [a]

	ΔH_f^0(298.15 K, g) (kcal mole^{-1})	Ref.
Monochloro		
2	−28.6	1
3	−36.7	10
4	−34.9	10
Dichloro		
2,3	−40	1
2,4	−39	1
2,5	−42	1
2,6	−24	1
3,4	−47	1
3,5	−48	
Trichloro		
2,3,4	−49	
2,3,5	−52	
2,3,6	−36	
2,4,5	−51	1
2,4,6	−34	
3,4,5	−57	
Tetrachloro		
2,3,4,5	−59	
2,3,4,6	−43	
2,3,5,6	−46	
Pentachloro		
2,3,4,5,6	−54	10

[a] Except for values taken from ref. 10, all values have been estimated using the procedure described in this paper.

kcal mole^{-1}, is a case in point. This difference is too large to explain in terms of steric, hydrogen bonding, or van der Waals effects. One may suspect that there may be substantial uncertainties associated with the original data for all chlorinated aromatic molecules. However, inspection of Table 1 indicates that the uncertainty limits calculated for mixed second order effects (Cl, OH) are much larger than those attributed to second order effects for common substituents (Cl, Cl). Thus the problems with the original data base are most likely to be associated with the chlorinated phenols. As a consequence, there are larger uncertainties associated with the estimated heats of formation of the polychlorinated diphenyl ethers, dibenzofurans, phenols and dioxins, than there are with the estimated heats of formation of the PCB's. In Table 4 some examples of the calculated uncertainties for these compounds are presented. (Limits are calculated as ± the square root of the sum of the squared uncertainties associated with the effects reported in

TABLE 4

Gas phase heats of formation with uncertainty limits (referred to benzene for phenols, referred to unsubstituted compounds for others) estimated for some typical polychlorinated organic compounds

Compound	ΔH_f^0(298.15 K, g) (kcal mole^{-1})
2-Chlorodiphenylether	11 ± 5
2,3,4-Trichlorodiphenylether	−13 ± 6
2,3,4,6-Tetrachlorodiphenylether	−8 ± 8
3,5,3′,5′-Tetrachlorodiphenylether	−41 ± 4
2,3,4,2′6′-Pentachlorodiphenylether	−14 ± 9
2,4,6,3′,5′-Pentachlorodiphenylether	−26 ± 8
2,3,4,6,3′,4′-Hexachlorodiphenylether	−32 ± 8
2,3,6,2′,4′,5′-Hexachlorodiphenylether	−24 ± 9
2,3,4,5,3′,4′,5′-Heptachlorodiphenylether	−54 ± 7
2,3,4,5,2′,3′,4′,6′-Octachlorodiphenylether	−40 ± 10
4-Chlorodibenzofuran	19 ± 5
3,7-Dichlorodibenzofuran	−7 ± 3
2,4,6-Trichlorodibenzofuran	−7 ± 7
1,2,7-Trichlorodibenzofuran	−17 ± 4
2,3,6,7-Tetrachlorodibenzofuran	−16 ± 6
1,4,7,8-Tetrachlorodibenzofuran	−18 ± 6
1,2,6,7,8-Pentachlorodibenzofuran	−25 ± 7
1,2,4,7,9-Pentachlorodibenzofuran	−30 ± 7
1,2,3,6,7,8-Hexachlorodibenzofuran	−36 ± 7
2,5-Dichlorophenol	−42 ± 4
2,6-Dichlorophenol	−24 ± 7
2,3,5-Trichlorophenol	−52 ± 5
2,3,4,5-Tetrachlorophenol	−59 ± 5
2-Chlorobiphenyl	36 ± 0.6
2,3,4′-Trichlorobiphenyl	23 ± 0.9
2,3,4,6-Tetrachlorobiphenyl	21 ± 2
3,5,3′,5′-Tetrachlorobiphenyl	15 ± 1
2,3,4,2′,6′-Pentachlorobiphenyl	13 ± 2
2,4,6,3′,5′-Pentachlorobiphenyl	9 ± 1
2,3,4,6,2′,6′-Hexachlorobiphenyl	13 ± 3
2,3,6,2′,4′,5′-Hexachlorobiphenyl	8 ± 3
2,3,4,5,3′,4′,5′-Heptachlorobiphenyl	4 ± 2
2,3,4,5,2′,3′,4′,6′-Octachlorobiphenyl	2 ± 3
1-Chlorodibenzo-*p*-dioxin	−22 ± 6
2,7-Dichlorodibenzo-*p*-dioxin	−51 ± 5
1,3,8-Trichlorodibenzo-*p*-dioxin	−57 ± 7
1,2,3,9-Tetrachlorodibenzo-*p*-dioxin	−60 ± 9
1,2,8,9-Tetrachlorodibenzo-*p*-dioxin	−61 ± 9
1,2,3,6,7-Pentachlorodibenzo-*p*-dioxin	−76 ± 9
1,2,4,7,8-Pentachlorodibenzo-*p*-dioxin	−68 ± 10
1,2,4,6,7,9-Hexachlorodibenzo-*p*-dioxin	−90 ± 12

Table 1 and the literature values as reported for the heats of formation for some of the reference compounds given in Table 2).

In summary, the magnitude of the uncertainties is such that variations in the estimated heats of formation for isomers of these compounds may not be represented accurately enough for many classes of problems, e.g. ambient equilibrium distributions in the environment. This is because in these instances equilibrium calculations of isomer distributions are sensitive to differences in heats of formation. All of these contributions (heats of formation data) for various isomers are characterized numerically by error limits which are substantial and which tend to be of about the same order of magnitude. In these equilibrium calculations there is no over-riding effect due to the contribution from CO_2 formation as is considered in combustion efficiency modeling. It would be very useful if thermodynamicists would measure additional (or even repeat determinations of) gas phase heats of combustion, formation or reaction of polychlorinated phenols. This would permit a refinement of the estimated values presented here, and thus extend the usefulness of this data.

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