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PROCEDURE FOR ESTIMATING THE HEATS OF FORMATION OF AROMATIC COMPOUNDS: CHLORINATED BENZENES, PHENOLS AND DIOXINS

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ABSTRACT

A method for estimating the gas phase heats of formation of some aromatic organic compounds is applied. A critical comparison of the gas phase heats of formation predicted by this method with the gas phase heats of formation reported experimentally for several aromatic organic compounds is presented. Practical applications of this method are illustrated for chlorinated dioxins, chlorinated phenols and chlorinated or fluorinated benzene molecules. The limitations and practical extensions of the method are discussed. The method is shown to be simple and of practical usefulness, particularly when required experimental data are unavailable.

INTRODUCTION

The availability of thermodynamic data is of fundamental importance, for example, as a tool for investigating and understanding many problems of considerable importance associated with practical combustion (e.g., propellant behavior in various propulsion devices, destruction of waste materials in incinerators, uniform pricing standards for various fuels, etc.). There are, at the present time, a number of very useful thermodynamic data compilations available for this purpose [1–4]. Often, however, information is required about compounds for which no experimental data have yet been generated. When such is the case, in lieu of performing experiments, it is then necessary to generate the data via some appropriate and preferably simple theoretical estimation scheme. Methodology for this purpose is available for application to many classes of chemical compounds [5–17]. The extent to which these methods are useful has been critically reviewed in the literature [3,18], and the reader is referred to the afore-mentioned excellent references. To a considerable extent, Benson's group method [18] has been very useful for estimating heats of formation of aromatic compounds, including some tabular information for making corrections for substituent neighbor interaction effects. The intent of this paper is to provide an additional estimation scheme methodology which will make possible the generation of theoretical thermodynamic data for the heats of formation of many more aromatic organic compounds.

A comparison of thermodynamic data developed by this method to data reported in the literature will be presented to illustrate somewhat the extent to which it should be possible to make reasonably reliable estimates. Several examples will be presented for the calculation of heats of formation of chlorinated benzenes, chlorinated phenols and chlorinated dibenzo-*p*-dioxins (dioxins). Note, all heats of formation reported here are for the gas phase at 298 K. (In this paper "heat of formation" is equivalent to "enthalpy of formation".) These are compounds which are known to be either precursors which can lead, under appropriate conditions, to the formation of toxic substances, or which are themselves (dioxins) extremely toxic substances [19]. There has in fact been considerable public attention and concern as to the efficiency of destruction of these materials under practical incineration conditions. For example, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, the most toxic of the dioxins, has been reported to have been found at parts-per-trillion level in fly ash effluents from municipal incinerators [19]. In this respect, it is clear that a kinetic and thermodynamic data base would be extremely useful. The work presented here is in response to a congressional mandate, and as directed under Section 5002 of the Resource Conservation Recovery Act of 1976 [RCRA], and through support of the NBS Office of Recycled Materials, and the DOE Office of Energy for Municipal Waste.

METHODOLOGY

The gas phase heats of formation for a number of organic compounds have been reported in the literature [1–4], and data for several specific compounds are presented in Table 1. Notably absent are data for tri-, tetra- and pentachlorinated benzenes, as well as a number of multichlorinated phenols. There are no data for dioxins.

A sensible approach towards estimation of the gas phase heats of formation for the above absent compounds is to start with a model molecule having a well-known gas phase heat of formation. In the case of aromatics, benzene is an obvious choice. What is then required is a procedure for determining the variation of the value of the gas phase heat of formation as heavier substituent (x) groups (e.g., chlorine in chlorobenzene) replace the hydrogen atoms attached to the benzene ring. Two major effects can be visualized: (a) the primary effect of replacing a hydrogen atom with x, and (b) the secondary effect of *ortho*-, *meta*- and *para*-x group interactions as in *ortho*-, *meta*- and *para*-dichlorobenzene, for example.

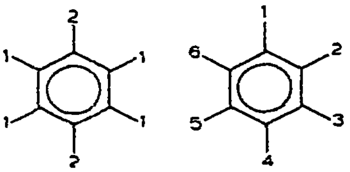


Fig. 1. (a) Two substituents. (b) Positional labeling.

TABLE 1

Thermodynamics data for some organic compounds

Compound	ΔH_f^0 (298, g) (kcal mole^{-1})	Ref.
Benzene	19.81 ± 0.13	3
Toluene	11.99 ± 0.10	3
o-Xylene	4.56 ± 0.26	3
m-Xylene	4.14 ± 0.18	3
p-Xylene	4.31 ± 0.24	3
1,2,3-Trimethyl benzene	−2.26 ± 0.29	3
1,2,4-Trimethyl benzene	−3.31 ± 0.26	3
1,3,5-Trimethyl benzene	−3.81 ± 0.33	3
1,2,3,4-Tetramethyl benzene	−10.02	2
1,2,3,5-Tetramethyl benzene	−10.71	2
1,2,4,5-Tetramethyl benzene	−10.82	2
Pentamethyl benzene	−17.80	2
Hexamethyl benzene	−20.75 ± 0.62	3
Chlorobenzene	12.21 ± 0.16	3
o-Dichlorobenzene	7.1 ± 0.4	3
m-Dichlorobenzene	6.1 ± 0.5	3
p-Dichlorobenzene	5.3 ± 0.3	3
Hexachlorobenzene	−8.6 ± 2.3	3
Fluorobenzene	−27.76 ± 0.29	3
o-Difluorobenzene	−70.26 ± 0.13	3
m-Difluorobenzene	−73.96 ± 0.17	3
p-Difluorobenzene	−73.33 ± 0.17	3
Pentafluorobenzene	−193.59 ± 0.35	3
Hexafluorobenzene	−228.49 ± 0.29	3
Phenol	−23.04 ± 0.21	3
Hydroquinone	−63.38 ± 0.50	3
Resorcinol	−65.7 ± 0.50	4
m-Chlorophenol	−36.7 ± 2.1	3
p-Chlorophenol	−34.9 ± 2.1	3
Pentachlorophenol	−53.9 ± 0.9	3
1,4-Dihydroxy-2-chlorobenzene	−75.0 ± 2.8	3
1,4-dihydroxy-2,6-dichlorobenzene	−79.3 ± 2.8	3
1,4-Dihydroxytetrachlorobenzene[a]	−81.2 ± 2.8	3
Biphenyl	43.53 ± 0.6	3
Biphenylene	115.2 ± 1.5	3
9,10-Dihydroanthracene	38.2 ± 1.1	3
Diphenylmethane	36.8 ± 0.5	3
Diphenylether	11.94 ± 0.67	3
Dibenzopyran	11.6 ± 1.2	3
Dibenzofuran	19.9 ± 1.2	3

[a] See note added in proof, p. 72.

By way of illustration of how a knowledge of these primary and secondary effects may be used to determine the gas phase heat of formation of an as yet uncharacterized compound, consider the hypothetical molecule shown in Fig. 1(a), in which two different substituents (1, 2) have totally replaced the hydrogen atoms on a benzene ring. We can denote the primary effect upon the gas phase heat of formation of benzene, due to replacement of a hydrogen atom with substituent 1, by the symbol, χ, and similarly the primary effect associated with substituent 2 by the symbol, β. The secondary *ortho*, *meta* and *para* effects can be respectively denoted by the symbols, o, m and p. These can be further doubly subscripted to indicate which substituents are interacting. For example, o_{12} denotes the *ortho* interaction of substituent 1 with substituent 2. With this formalism, the gas phase heat of formation of the uncharacterized compound, $\Delta H_f^0(?)$, can be derived from a knowledge of the gas phase heat of formation of benzene, $\Delta H_f^0(C_6H_6)$, as follows

$$\Delta H_f^0(?) = \Delta H_f^0(C_6H_6) - [4\chi + 2\beta] + 4o_{21} + 4m_{21} + p_{22} + 2(o_{11} + m_{11} + p_{11})$$

Above, the primary substituent effect correction is fairly obvious. To see how the secondary effects have been determined, it is necessary to observe the positional labeling shown for the hypothetical molecule, as in Fig. 1(b). The possible positional interactions are determined (clockwise examination) to be

(12, 13, 14, 15, 16), (23, 24, 25, 26), (34, 35, 36), (45, 46), 56

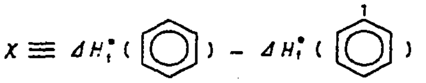
If we retain the positional interaction indices as superscripts and identify each interaction as *ortho*, *meta* or *para*, then the interactions can be written as

$$o^{12}, m^{13}, p^{14}, m^{15}, o^{16}, o^{23}, m^{24}, p^{25}, m^{26}, o^{34}, m^{35}, p^{36}, o^{45}, m^{46}, o^{56}$$

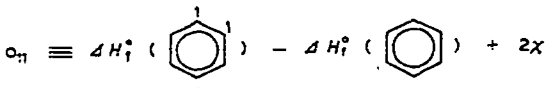
We can now, via subscripts, label the interactions according to the nature of the substituent, drop the superscripts and group the common interactions. These operations result in a final assignment of the secondary effects

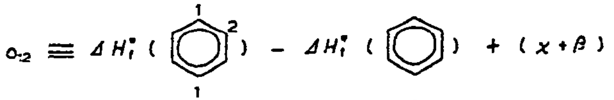
$$4o_{21} + 4m_{21} + p_{22} + 2(o_{11} + p_{11} + m_{11})$$

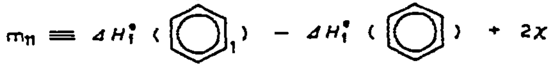
What remains to be determined is how to calculate numerical values of the primary and secondary interaction effects. This is done as follows. The primary effect correction for substituent 1 on benzene is defined schematically as

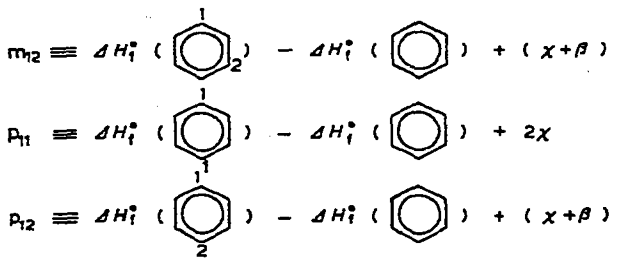


Second order corrections are then defined schematically as:









The positional interactions for di-, tri-, tetra-, penta- and hexa-substituted benzenes are presented in Table 2 as are the resulting secondary effects obtained for a common substituent in all substituted positions.

As a test of the applicability of this method for estimating heats of formation, the primary and secondary effects have been calculated, as defined above, for methyl

TABLE 2

Positional interactions: common substituents on benzene ring

Substituents	Interactions	Net secondary effect
ortho-	12	*o*
meta-	13	*m*
para-	14	*p*
1,2,3-Tri-	12, 13, 23	2*o*+*m*
1,2,4-Tri-	12, 14, 24	*o*+*m*+*p*
1,3,5-Tri	13, 15, 35	3*m*
1,2,3,4-Tetra-	12, 13, 14, 23, 24, 34	3*o*+2*m*+*p*
1,2,3,5-Tetra-	12, 13, 15, 23, 25, 35	2*o*+3*m*+*p*
1,2,4,5-Tetra-	12, 14, 15, 24, 25, 45	2*o*+2*m*+2*p*
Penta-	12, 13, 14, 15, 23, 24, 25, 34, 35, 45	4*o*+4*m*+2*p*
Hexa	12, 13, 14, 15, 16, 23, 24, 25, 26, 34, 35, 36, 45, 46, 56	6*o*+6*m*+3*p*

TABLE 3

Calculated and literature values for heats of formation of substituted benzenes (kcal mole^{-1})

Substitution	$-CH_3$		$-Cl$		$-F$	
	Calcd.	Lit.	Calcd.	Lit.	Calcd.	Lit.
1,2,3-	−2.73	−2.26±0.29	2.18		−111.39	
1,2,4-	−3.15	−3.31±0.26	0.48		−114.46	
1,3,5-	−3.74	−3.81±0.33	−0.02		−118.79	
1,2,3,4-	−10.22	−10.02	−1.95		−150.52	
1,2,3,5-	−10.64	−10.71	−3.05		−154.22	
1,2,4,5-	−10.47	−10.82	−3.65		−153.59	
Penta-	−17.72	−17.80	−5.09		−188.28	−193.59±0.35
Hexa-	−24.53	−20.75±0.62	−6.14	−8.6±2.3	−220.97	−228.49±0.29

substituted benzene compounds, for which (Table 1) experimental data have been reported in the literature. Primary and secondary effect corrections have been used, according to the methodology described above, to estimate the gas phase heats of formation of the tri-, tetra-, penta- and hexa-methyl substituted benzenes. The comparison between the estimated gas phase heats of formation and those values reported in the literature is seen to be quite reasonable, as is shown in Table 3.

APPLICATIONS

Substituted benzene compounds—common substituents

There is enough thermodynamic data for gas phase heats of formation so that it is possible to estimate the values of the tri-, tetra-, penta- and hexa-substituted methyl-, chloro- and fluorobenzenes. Values for the gas phase heats of formation of hydroquinone [3] and resorcinol [4] have been reported in the literature. However, a value for the gas phase heat of formation of pyrocatechol is not presently available. Thus, in the case of OH substituted benzene compounds, only a value for the gas phase heat of formation of phloroglucinol (1,3,5-substituted) can be estimated. Possible estimations for alkyl substituted benzene molecules, where the alkyl substituents are other than methyl, can be determined by reference to existing thermodynamics data bases [1–4]. The reader is referred to Table 3 for a summary of estimated gas phase heats of formation of chloro-, fluoro- and hydroxy-substituted benzene compounds. Lower experimental limit values for the heats of formation of the dichlorobenzenes have been used in calculating secondary effects. This choice permits reasonable agreement with the reported experimental value for hexachlorobenzene and results in the expected decreasing trend in the heats of formation with increasing chlorination. Note that, as data are or become available for mono- and di-substituted naphthalene and anthracene, analogous methodology may be used to estimate multiple substituent effects in these compounds. Alternatively, the substituent effects associated with benzene may, as an approximation, be used for multiple ring compounds.

Chlorinated phenols

It is seen from examination of Table 1 that thermodynamic data are available for the gas phase heats of formation of a few chlorinated phenols. As reported in a recent EPA document [19], there are several chlorinated phenols which are known to be precursors to the formation of chlorinated dioxins. Therefore it is useful, where thermodynamic data are not presently available, to estimate gas phase heats of formation for the purpose of making, in the future, estimates of the relative equilibrium thermal stability of these compounds when other requisite thermodynamic data (heat capacity and entropy) become available. The gas phase heats of formation for phenol and benzene, as reported in Table 1, may be used to determine the primary substituent effect when an OH group replaces a hydrogen atom in a benzene ring. The second order mixed chloro-/hydroxy-substituent effects for the p_{12}, p_{22} and m_{12} interactions may be respectively determined from *p*-chlorophenol, hydroquinone and *m*-chlorophenol. There are three model compounds reported in Table 1 which may be used to determine the o_{12} effect for the case where the OH group is simultaneously *ortho* to two chlorine substituents. These compounds are penta-chlorophenol, 1,4-dihydroxy-2,6-chlorobenzene and 1,4-dihydroxytetrachlorobenzene. For the case where the OH group is *ortho* only to one chlorine substituent, the model compound for determination of the o_{12} effect is 1,4-dihydroxy-2-chlorobenzene. This distinction is made to differentiate between the former case, where the competitive effect of two *ortho*-chlorine substituents is likely to raise the gas phase heat of formation of the molecule, and the latter 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 is likely to lower the estimated gas phase heat of formation of the molecule. Since there are three possible model compounds for the former case, I have chosen an average of the three computed values for the o_{12} effect. The *o*, *m*, and *p* effects for common and mixed substituents are summarized in Table 4. Table 5 summarizes the estimated gas phase heats of formation for a number of chlorinated phenols which are regarded to be dioxin precursors [19].

As regards the data presented in Tables 3 and 4, it is instructive to make the following observations. The heats of formation which are presented in Table 3 are based upon calculations which consider primary substituent and secondary (*ortho, meta* and *para*) interaction effects. These calculated values are seen to agree with those reported in the literature on the average to within less than a kcal except for the totally substituted species. Numerical values attributable to primary substituent

TABLE 4[a]

Summary of (χ, o, m, p) effects (kcal mole^{-1})

Effect	$-CH_3$	$-Cl$ (1)	$-F$	$-OH$ (2)
χ	7.82	7.6	47.57	42.85
o	0.39	2.09	5.07	
m	−0.03	0.99	1.37	0.19
p	0.14	0.39	2.00	2.51
o_{12}(I)		−0.47	(OH adjacent to one Cl atom)	
o_{12}(II)		5.96	(OH symmetrically surrounded by Cl)	
m_{12}		−6.06		
p_{12}		−4.26		

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[a] See note added in proof, p. 72.

All interaction effects except the o_{12}(I) effect have been determined from benzene as a reference compound. In this paper, the o_{12}(I) effect was determined from hydroquinone as a reference compound.

TABLE 5 [a]

Calculated heats of formation for some chlorinated phenols

	Calculation	ΔH_f^0(298, g) (kcal mole^{-1})
2,4,5-Trichlorophenol	$B-3\chi-\beta+o_{12}(\mathrm{I})+p_{12}+m_{12}+o_{11}+m_{11}+p_{11}$	−53.16
ortho-Chlorophenol	$B-\chi-\beta+o_{12}(\mathrm{I})$	−31.11
3,4-Dichlorophenol	$B-2\chi-\beta+m_{12}+p_{12}+o_{11}$	−46.47
Chlorohydroquinone	$B-\chi-2\beta+o_{12}(\mathrm{I})+m_{12}+p_{22}$	−77.51
2,3-Dichlorophenol	$B-2\chi-\beta+o_{12}(\mathrm{I})+m_{12}+o_{11}$	−42.68
2,4-Dichlorophenol	$B-2\chi-\beta+o_{12}(\mathrm{I})+p_{12}+m_{11}$	−41.98
2,5-Dichlorophenol	$B-2\chi-\beta+o_{12}(\mathrm{I})+m_{12}+p_{11}$	−44.23
2,6-Dichlorophenol	$B-2\chi-\beta+2o_{12}(\mathrm{II})+m_{11}$	−25.33

$B \equiv \Delta H_f^0$(benzene); $\chi \equiv$ primary effect (Cl); $\beta \equiv$ primary effect (OH); subscript 1 denotes Cl; subscript 2 denotes OH.

[a] See note added in proof, p. 72.

and secondary interaction effects have been determined from a consideration of a somewhat limited set of model compounds. Prosen et al. [20] have, in the past, developed an estimation scheme for alkyl substituted benzenes in which primary substituent and second order effects have been determined from a more extensive set of compounds as a data base. The reported primary and secondary substituent effects corrections they determined differ from those reported here in Table 4. The reader is cautioned to exercise care in interpreting these differences. Aside from algebraic sign variations attributable to the slightly dissimilar character of the equation formalisms used in computing the heats of formation, Prosen has used a value for the phenyl group which differs from that reported in the literature [3]. This is a consequence of the least squares method of fitting that was used. Thus, the method reported here and the derived substituent effects are used as exact corrections to the molecule benzene, while in the case of Prosen's method the substituent correction effects are convoluted into coefficients used in a least squares equation not explicitly related to benzene in particular. In general, one should not interchange the use of substituent effects corrections reported here and in Prosen's paper between the two equations of the former and later methods for computing gas phase heats of formation. As regards Prosen's method, the primary advantage to be expected derives from reference to a more extensive set of compounds. The choice of a more extensive set as a basis for computing substituent effects was not made here, as I am primarily concerned with chloro-substituted aromatics, for which more extensive compound data is simply not available at the present time. Thus the limits of the basis set are dictated by the chloro-compound heat of formation literature. Therefore the choice of data for computing methyl substituent effects has correspondingly been limited to permit the reader by direct analogy to understand the typical error limits to be expected for estimated gas phase heats of formation of chloro-compounds via use of this more limited data base.

More recently, Good [21] has reported a weighted least squares method, also referenced to a more extensive data base of alkyl substituted aromatic compounds than has been used in this report. The same precautionary statements regarding direct comparison of parameters as per Prosen's work discussed above apply here also. The primary advantage of Good's method is attributable to reference to a more extensive data base of compounds. The standard deviation in the comparison of gas phase heats of combustion between experiment and Good's method determined for methyl substituted benzenes through tetra-substitution is 0.117 kcal mole^{-1}. The standard deviation for gas phase heats of formation for the same compounds, in comparing literature reports with the results from the method I outlined here, is 0.195 kcal mole^{-1}.

It should be noted that Good concluded that within the construct of his method, as applied to methyl substitution, there are no (statistically admissible) *ortho-* or *para*-substituent effects, but that there is a "buttress" (1, 2, 3) effect. Again, interchange of parameters between equations is inadvisable. For example, the method I use here requires an exact fit of the gas phase heat of formation to all alkyl substituted benzene compounds up through di-substitution. In this case, the "buttress" (1, 2, 3) effect is determined for methyl groups to be 0.47 ± 0.29 kcal mole^{-1} compared to Good's reported value of 0.9961 ± 0.0608 kcal mole^{-1}. As I mentioned previously, gas phase heats of formation data for chloro-substituted aromatics is very limited. Thus Good's method was not used at the present time. I have for the same reason, not been able to compute a "buttress" (1, 2, 3) effect for chlorine substitution via the method I have outlined.

Benson's method provides some data for mono- and *ortho*-substitution by both chloro and methyl substituents. Agreement between his parameters and those reported here are consistently within considerably less than a value of 1 kcal mole^{-1}. Differences may be attributable to use of exact values for the gas phase heats of formation of compounds, as referenced in this report. Benson's method was not used here, as only an *ortho* effect for chlorine substitution has been reported by him.

In summary, there are other methods available which, as they are referenced to more extensive sets of compounds, are more desirable to apply. However, in the case of chlorine substitution, adequate data are not available at the present time to permit application of these methods. For those persons wishing to use the gas phase heats of formation I report here towards development of thermodynamic functions for equilibrium modeling as applied to the practical combustion problems alluded to at the beginning of this paper, the uncertainty in the values reported here is not serious. This is because in practical high temperature combustion, the primary driving force in the destruction of large carbon based organic molecules is primarily controlled by the stoichiometric coefficient associated with carbon dioxide formation.

Estimation of the gas phase heat of formation of dibenzo-p-dioxin

The gas phase standard heats of formation of 9,10-dihydroanthracene [Fig. 2(a)] and dibenzopyran [Fig. 2(b)] are reported in Table 1. I will assume that the effect of replacing a $-CH_2-$ group in 9,10-dihydroanthracene with an $-O-$ group, as in dibenzopyran, is given by the difference, D, in the gas phase heats of formation of the former and latter compounds

$$D = \Delta H_f^0(C_{14}H_{12}) - \Delta H_f^0(C_{13}H_{10}O) = 26.6 \text{ kcal}$$

Above, it is seen that replacing a $-CH_2-$ group with an $-O-$ group lowers the gas

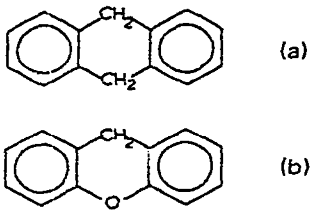

Fig. 2. (a) 9,10-Dihydroanthracene. (b) Dibenzopyran.

phase heat of formation. The gas phase heat of formation of dibenzo-*p*-dioxin (dioxin), as shown in Fig. 3(a), may therefore be estimated as

$$\Delta H_f^0(\text{dibenzo-}p\text{-dioxin}) \approx \Delta H_f^0(C_{13}H_{10}O) - D \approx -15.0 \text{ kcal}$$

Estimated gas phase heats of formation for chlorinated dioxins

The following formalism will be used to estimate the gas phase heats of formation for chlorinated dioxins. (Note that analogously as to be outlined here for dioxins, the gas phase heats of formation for chlorinated dibenzofurans may also be estimated, as a value for the gas phase heat of formation of dibenzofuran has already been reported in the literature and is noted in Table 1.)

The procedure for estimating the gas phase heat of formation for chlorinated dioxins will be by way of an example calculation for the compound, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), shown in Fig. 3b. I will assume that, as a first approximation:

(a) "*meta*-" and "*para*" effects of the (–Cl) and (–O–) group interactions may be ignored;

(b) replacement of an (–H) group with a (–Cl) group in dioxin is roughly equivalent to the same replacement on benzene;

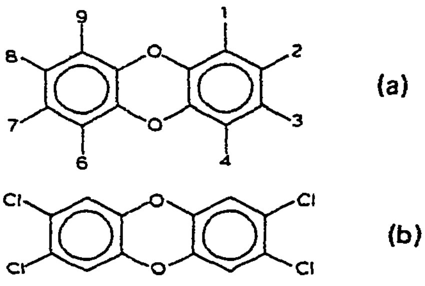

Fig. 3. (a) Dibenzo-*p*-dioxin, (b) 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin.

TABLE 6[a]

Calculated heats of formation of chlorinated dioxins

Dioxin	Calculation	ΔH_f^0 (298, g) (kcal mole^{-1})
1-Chlorodibenzo-*p*-dioxin	$DD-\chi+o_{12}+m_{12}$	−22.7
2-Chlorodibenzo-*p*-dioxin	$DD-\chi+m_{12}+p_{12}$	−32.92
1,2-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2m_{12}+o_{12}+o_{11}+p_{12}$	−38.53
1,3-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2m_{12}+m_{11}+o_{12}+p_{12}$	−39.63
1,4-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2(o_{12}+m_{12})+p_{11}$	−30.01
1,6-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2(o_{12}+m_{12})$	−30.4
1,7-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2m_{12}+o_{12}+p_{12}$	−40.62
1,8-Dichlorodibenzo-*p*-dioxin	=1,7-DCDD	
1,9-Dichlorodibenzo-*p*-dioxin	=1,6-DCDD	
2,3-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2(m_{12}+p_{12})+o_{11}$	−48.75
2,7-Dichlorodibenzo-*p*-dioxin	$DD-2\chi+2(m_{12}+p_{12})$	−50.84
2,8-Dichlorodibenzo-*p*-dioxin	=2,7-DCDD	
1,2,3-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2(p_{12}+o_{11})+o_{12}+m_{11}$	−53.37
1,2,4-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2o_{12}+p_{12}+o_{11}+m_{11}+p_{11}$	−44.85
1,2,6-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2o_{12}+p_{12}+o_{11}$	−46.23

TABLE 6 (continued)

Dioxin	Calculation	ΔH_f^0 (298, g) (kcal mole^{-1})
1,2,7-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2p_{12}+o_{12}+o_{11}$	−56.45
1,2,8-Trichlorodibenzo-*p*-dioxin	= 1,2,7-TCDD	
1,2,9-Trichlorodibenzo-*p*-dioxin	= 1,2,6-TCDD	
1,3,6-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2o_{12}+p_{12}+m_{11}$	−47.33
1,3,7-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2p_{12}+o_{12}+m_{11}$	−57.55
1,3,8-Trichlorodibenzo-*p*-dioxin	= 1,3,7-TCDD	
1,3,9-Trichlorodibenzo-*p*-dioxin	= 1,3,6-TCDD	
1,4,6-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3(o_{12}+m_{12})+p_{11}$	−37.71
1,4,7-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3m_{12}+2o_{12}+p_{12}+p_{11}$	−47.93
2,3,6-Trichlorodibenzo-*p*-dioxin	= 1,2,7-TCDD	
2,3,7-Trichlorodibenzo-*p*-dioxin	$DD-3\chi+3(m_{12}+p_{12})+o_{11}$	−66.67
1,2,3,4-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3o_{11}+2(o_{12}+p_{12}+m_{11})+p_{11}$	−57.6
1,2,3,6-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12}+o_{11})+m_{11}$	−61.07
1,2,3,7-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3p_{12}+2o_{11}+o_{12}+m_{11}$	−71.29
1,2,3,8-Tetrachlorodibenzo-*p*-dioxin	= 1,2,3,7-TCDD	
1,2,3,9-Tetrachlorodibenzo-*p*-dioxin	= 1,2,3,6-TCDD	
1,2,4,6-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3o_{12}+p_{12}+o_{11}+m_{11}+p_{11}$	−52.55
1,2,4,7-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12})+o_{11}+m_{11}+p_{11}$	−62.77
1,2,4,8-Tetrachlorodibenzo-*p*-dioxin	= 1,2,4,7-TCDD	
1,2,4,9-Tetrachlorodibenzo-*p*-dioxin	= 1,2,4,6-TCDD	
1,2,6,7-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12}+o_{11})$	−62.06
1,2,6,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12})+o_{11}+m_{11}$	−63.16
1,2,6,9-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3o_{12}+p_{12}+o_{11}+p_{11}$	−53.54
1,2,7,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3p_{12}+2o_{11}+o_{12}$	−72.28
1,2,7,9-Tetrachlorodibenzo-*p*-dioxin	= 1,2,6,8-TCDD	
1,2,8,9-Tetrachlorodibenzo-*p*-dioxin	= 1,2,6,7-TCDD	
1,3,6,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12}+m_{11})$	−64.26
1,3,6,9-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3o_{12}+p_{12}+m_{11}+p_{11}$	−54.64

1,3,7,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+3p_{12}+o_{12}+m_{11}+o_{11}$	−73.38
1,3,7,9-Tetrachlorodibenzo-*p*-dioxin	=1,3,6,8-TCDD	
1,4,6,9-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4(m_{12}+o_{12})+2p_{11}$	−45.02
1,4,7,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4m_{12}+2(o_{12}+p_{12})+p_{11}+o_{11}$	−63.76
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	$DD-4\chi+4(m_{12}+p_{12})+2o_{11}$	−82.5
1,2,3,4,6-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3(o_{12}+o_{11})+2(p_{12}+m_{11})+p_{11}$	−65.3
1,2,3,4,7-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3(p_{12}+o_{11})+2(o_{12}+m_{11})+p_{11}$	−75.52
1,2,3,6,7-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3(p_{12}+o_{11})+2o_{12}+m_{11}$	−76.9
1,2,3,6,8-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3p_{12}+2(o_{12}+o_{11}+m_{11})$	−78.0
1,2,3,6,9-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3o_{12}+2(p_{12}+o_{11})+m_{11}+p_{11}$	−68.38
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+4p_{12}+3o_{11}+o_{12}+m_{11}$	−87.12
1,2,3,7,9-Pentachlorodibenzo-*p*-dioxin	=1,2,3,6,8-PCDD	
1,2,3,8,9-Pentachlorodibenzo-*p*-dioxin	=1,2,3,6,7-PCDD	
1,2,4,6,7-Pentachlorodibenzo-*p*-dioxin	=1,2,3,6,9-PCDD	
1,2,4,6,8-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3o_{12}+2(p_{12}+m_{11})+o_{11}+p_{11}$	−69.48
1,2,4,6,9-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+4o_{12}+2p_{11}+p_{12}+o_{11}+m_{11}$	−59.86
1,2,4,7,8-Pentachlorodibenzo-*p*-dioxin	$DD-5\chi+5m_{12}+3p_{12}+2(o_{12}+o_{11})+m_{11}+p_{11}$	−78.6
1,2,4,7,9-Pentachlorodibenzo-*p*-dioxin	=1,2,4,6,8-PCDD	
1,2,4,8,9-Pentachlorodibenzo-*p*-dioxin	=1,2,3,6,9-PCDD	
1,2,3,4,6,7-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+4o_{11}+3(p_{12}+o_{12})+2m_{11}+p_{11}$	−81.13
1,2,3,4,6,8-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+3(p_{12}+o_{11}+m_{11}+o_{12})+p_{11}$	−82.23
1,2,3,4,6,9-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+4o_{12}+3o_{11}+2(p_{12}+m_{11}+p_{11})$	−72.61
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+4(p_{12}+o_{11})+2(m_{11}+o_{12})+p_{11}$	−91.35
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+4(o_{11}+p_{12})+2(o_{12}+m_{11})$	−91.74
1,2,3,6,7,9-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+3(o_{12}+p_{12}+o_{11})+2m_{11}+p_{11}$	−83.22
1,2,3,6,8,9-Hexachlorodibenzo-*p*-dioxin	=1,2,3,6,7,9-HCDD	
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	=1,2,3,6,7,8-HCDD	
1,2,4,6,7,9-Hexachlorodibenzo-*p*-dioxin	$DD-6\chi+6m_{12}+4o_{12}+2(p_{12}+o_{11}+m_{11}+p_{11})$	−74.7
1,2,4,6,8,9-Hexachlorodibenzo-*p*-dioxin	=1,2,4,6,7,9-HCDD	
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin	$DD-7\chi+7m_{12}+5o_{11}+4p_{12}+3(o_{12}+m_{11})+p_{11}$	−95.97
1,2,3,4,6,7,9-Heptachlorodibenzo-*p*-dioxin	$DD-7\chi+7m_{12}+4(o_{11}+o_{12})+3(p_{12}+m_{11})+2p_{11}$	−87.45
Octachlorodibenzo-*p*-dioxin	$DD-8\chi+8m_{12}+6o_{11}+4(o_{12}+p_{12}+m_{11})+2p_{11}$	−100.2

$DD\equiv\Delta H_f^0$(dibenzo-*p*-dioxin); $\chi\equiv$ primary effect (Cl); subscript 1 denotes Cl; subscript 2 denotes OH.

[a] See note added in proof, p. 72.

(c) the (–Cl) *ortho* effect in benzene is the same in 2,3,7,8-TCDD.
Then, as a first approximation (dioxin is denoted DD below)

$$\Delta H_f^0(2,3,7,8\text{-TCDD}) \approx \Delta H_f^0(\text{DD}) - 4\chi_{\text{Cl}} + 2o_{\text{Cl,Cl}} \approx -41.22\ \text{kcal}$$

However, we must now correct for the "*meta*-" and "*para*" effects of the (–Cl) and (–O) group interactions in 2,3,7,8-TCDD. To do this we will assume: (i) the "*meta*" effect is equivalent to the *meta* effect associated with *m*-chlorophenol, and (ii) the "*para*" effect is equivalent to the *para* effect associated with *p*-chlorophenol. There are some chlorinated dioxins for which a knowledge of the "*ortho*" effect is required. It will be assumed equivalent to the average *ortho* effect associated with the compounds: pentachlorophenol, 1,4-dihydroxytetrachlorobenzene and 1,4-dihydroxy -2,6-dichlorobenzene. These *o*-, *m*- and *p*-mixed substituent effects have been calculated following the methodology I have previously described and are reported in Table 4. With corrections, for these additional effects the gas phase heat of formation for 2,3,7,8-TCDD can be estimated as

$$\Delta H_f^0(2,3,7,8\text{-TCDD}) \approx \Delta H_f^0(\text{DD}) - 4\chi_{\text{Cl}} + 2o_{\text{Cl,Cl}} + 4(p_{\text{OH,Cl}} + m_{\text{OH,Cl}})$$
$$\approx -82.5\ \text{kcal}$$

The gas phase heats of formation of the other 74 possible chlorinated dioxins can be similarly estimated, and the calculations are presented in Table 6. As noted previously, a similar table may be easily generated for chlorinated dibenzofurans. As regards the chlorinated dioxins, a careful examination of Table 6 leads to two tentative conclusions that: (i) the primary effect of increased chlorination is a lowering of the gas phase heat of formation, and (ii) the more the number of chlorine atoms in the "*ortho*" position to the –O– group, the more the gas phase heat of formation is raised.

NOTE ADDED IN PROOF

In the body of the paper and in Table 1, the compound 1,4-dihydroxytrichlorobenzene is incorrectly identified as 1,4-dihydroxytetrachlorobenzene. When this correction is taken into account, it is necessary to correct the value reported for the o_{12}(II) effect from 5.96 kcal mole^{-1} to 6.83 kcal mole^{-1} in Table 4. The reader is further instructed that where the o_{12}(II) effect is incorporated into Tables 5 and 6, corresponding adjustments should be made by performing the calculations indicated in the tables.

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REFERENCES

1 D.R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd edn., NSRDS-NBS 37, National Bureau of Standards, Washington, DC, 1971.
2 D.R. Stull, E.F. Westrum, Jr. and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, John Wiley and Sons, New York, 1969.
3 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.
4 J.B. Pedley and J. Rylance, Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, Brighton, Gt. Britain, 1977.
5 G.S. Parks and H.M. Huffman, Free Energies of Some Organic Compounds, Am. Chem. Soc. Monogr. No. 60, The Chemical Catalog Co., New York, 1932.
6 F.D. Rossini, J. Res. Natl. Bur. Stand., 13 (1934) 21.
7 E.J. Prosen, W.H. Johnson and F.D. Rossini, J. Res. Natl. Bur. Stand., 37 (1946) 51.
8 S.W. Benson and J.H. Buss, J. Chem. Phys., 29 (1958) 546.
9 K.J. Laidler, Can. J. Chem., 34 (1956) 626.
10 V.M. Tatevskii, V.A. Benderskii and S.S. Yarovoi, Rules and Methods for Calculating the Physicochemical Properties of Paraffinic Hydrocarbons (translation Ed. B.P. Mullins), Pergamon Press, Oxford, 1961.
11 J.B. Greenshields and F.D. Rossini, J. Phys. Chem., 62 (1958) 271.
12 G.R. Somayajulu and B.J. Zwolinski, Trans. Faraday Soc., 62, (1966) 2327.
13 H. Lehmann and E. Ruschitzky, Chem. Tech. (Berlin), 19 (1967) 226.
14 S.E. Stein and B.D. Barton, Thermochim. Acta. 44 (1981) 265.
15 H.K. Eigenmann, D.M. Golden and S.W. Benson, J. Phys. Chem., 77 (1973) 1687.
16 H.E. O'Neal and S.W. Benson, J. Chem. Eng. Data, 15 (1970) 266.
17 H.E. O'Neal and S.W. Benson, in J.K. Kochi (Ed.), Free Radicals, Wiley, New York, 1973, Chap. 17.
18 S.W. Benson, Thermochemical Kinetics, 2nd edn., John Wiley and Sons, New York, 1976.
19 M.P. Esposito, T.O. Tiernan and F.E. Dryden, Dioxins, EPA-600/2-80-197, EPA Industrial Environmental Research Laboratory, Cincinnati, OH, 1980.
20 E.J. Prosen, W.H. Johnson and F.D. Rossini, J. Res. Natl. Bur. Stand., 36 (1946) 455.
21 W.D. Good, J. Chem. Thermodyn., 7 (1975) 49.