516 *J. Chem. Eng. Data* **1999,** *44,* 516−523

Thermodynamic Properties of Dibenzo-*p*-dioxin, Dibenzofuran, and Their Polychlorinated Derivatives in the Gaseous and Condensed Phases. 1. Thermodynamic Properties of Gaseous Compounds

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Gas-phase thermodynamic properties (enthalpy of formation, entropy, and heat capacity) are estimated for dibenzo-*p*-dioxin (DD), dibenzofuran (DF), 75 possible isomers of polychlorinated dibenzo-*p*-dioxins (PCDDs), and 135 of polychlorinated dibenzofurans (PCDFs). To estimate the enthalpy of formation values, the difference method is used that is completely consistent with the group additivity approach. Entropies and heat capacities are calculated by statistical thermodynamics using evaluated structural parameters and vibrational frequencies. Normal coordinate analysis is carried out for all isomers of PCDDs and PCDFs by transferring the force constants from polycyclic aromatic hydrocarbons, dibenzofuran, and chlorinated benzenes. The group additivity scheme with 10 parameters is developed to approximate calculated thermodynamic properties. Results obtained in this work are compared with published experimental and theoretical data.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are considered to be among the most acutely toxic compounds in the environment. The availability of thermodynamic data for these compounds is of fundamental importance for understanding the mechanism of their formation in order to assist in the design of strategies to effectively control or eliminate their emissions.

A number of studies have been reported over the past 15 years which proposed the methods of prediction of the thermodynamic properties of gaseous PCDDs and PCDFs (Shaub, 1982a,b, 1983; Koester and Hites, 1988; Fokin et al., 1989; Rordorf, 1989; Murabayashi and Moesta, 1992; Ritter and Bozzelli, 1994; Thompson, 1994a,b, 1995; Dorofeeva and Gurvich, 1996). The results of these predictions differ from one another substantially and that prohibits one from obtaining reliable data on the stability of PCDDs and PCDFs, conditions of their formation, and relative isomer distributions (Rordorf, 1989; Ritter and Bozzelli, 1994; Thompson, 1994a,b, 1995; Dorofeeva and Gurvich, 1996). Recent experimental determinations of enthalpy of formation of dibenzo-*p*-dioxin (DD) and some of its chlorinated derivatives (Kolesov et al., 1995, 1996; Papina et al., 1996; Lukyanova et al., 1997) as well as the experimental and theoretical investigations of vibrational spectra (Rauhut and Pulay, 1995; Klots and Collier, 1996; Sommer et al., 1997) make it possible to predict the values of enthalpy of formation, entropy, and heat capacity more plausibly. In this work the thermodynamic data for PCDDs and PCDFs are reexamined and compared with published results.

Enthalpies of Formation of Gaseous Compounds

Three values of enthalpy of formation, (83.4 ± 4.7) kJ·mol^{-1} (Cox and Pilcher, 1970; Pedley, 1994), (55.3 ± 0.3) kJ·mol^{-1} (Chirico et al., 1990), and (47.3 ± 4.8) kJ·mol^{-1} (Sabbah, 1991), were determined for gaseous dibenzofuran (DF) from experimental measurements. The value of (55.3 ± 0.3) kJ·mol^{-1} obtained by Chirico et al. (1990) from a more precise calorimetric investigation is recommended in this work. The values of the enthalpies of formation of dibenzo-*p*-dioxin (DD), 1-chlorodibenzo-*p*-dioxin (1-CDD), 2-chlorodibenzo-*p*-dioxin (2-CDD), and 2,3-dichlorodibenzo-*p*-dioxin (2,3-DCDD) were recently determined by Kolesov et al. (1995, 1996), Papina et al. (1996), and Lukyanova et al. (1997) from combustion calorimetry studies (Table 1). No experimental data are available for the other PCDDs and PCDFs.

Shaub (1982a, 1983) has developed a group contribution method to estimate the gas-phase enthalpies of formation of PCDDs and PCDFs. In addition to the effect of replacing a hydrogen atom with a chlorine atom, the author considered the *ortho*-, *meta*- and *para*-interactions between chlorine atoms and chlorine and oxygen atoms. The latter interactions were assumed to be the same as those in chlorinated phenols. However, the semiempirical calculations (Koester and Hites, 1988; Fokin et al., 1989), the recent estimations by additivity method (Thompson, 1994a, 1995; Dorofeeva and Gurvich, 1996) (Table 1) and predictions of relative concentrations of chlorinated dioxins and dibenzofurans (Thompson, 1994b; Unsworth and Dorans, 1993) indicate that Shaub's model is unsatisfactory. Because of strong oxygen−chlorine interactions suggested in this model, the value of the enthalpy of formation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is found to be much less (−345 kJ·mol^{-1}) than that estimated by other methods (from −160 to −190 kJ·mol^{-1}; see Table 1).

To estimate the enthalpies of formation of PCDDs and PCDFs, in our previous work (Dorofeeva and Gurvich, 1996) we used the difference method (Stull et al., 1969; Cohen and Benson, 1993; Dorofeeva and Tolmach, 1993) that is completely consistent with group additivity yet can sometimes offer a more accurate estimating scheme. The

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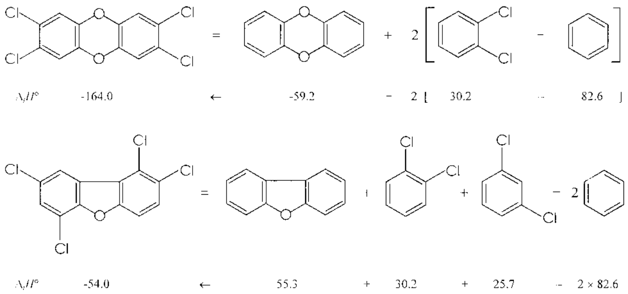
10.1021/je980238r CCC: $18.00 © 1999 American Chemical Society
Published on Web 04/17/1999

Table 1. Enthalpies of Formation for Gaseous DD, DF, PCDDs, and PCDFs

		$\Delta_f H°$(298.15 K)/(kJ·mol^{-1})								
		MNDO calc		est by group additivity approach						
molecule	expt	Koester and Hites (1988)	Fokin et al. (1989)	Shaub (1982a, 1983)	Murabayashi and Moesta (1992)	Ritter and Bozzelli (1994)	Thompson (1994b)	Thompson (1995)	Dorofeeva and Gurvich (1996)	this work
				Dibenzo-*p*-dioxin and Polychlorinated Dibenzo-*p*-dioxins						
DD	−59.2 ± 4.4[a]		−94.1	−62.8			−62.9	−55	−70	−59.2 ± 3.8[j]
1-CDD	−85.7 ± 7.0[b]			−95.0			−91.6[h]	−84.5	−100	−89.8 ± 10
2-CDD	−74.1 ± 3.3[c]			−137.7			−91.6[h]	−84.5	−100	−89.8 ± 10
2,3-DCDD	−119 ± 20[b]			−204.0			−120.0[h]	−106.5	−122	−112 ± 10
2,3,7,8-TCDD		−186.8	−187.0	−345.2	−338.9	−440.6	−171.1 [h]	−158.0	−175	−164 ± 15
1,2,3,6,7-PnCDD		−184.4		−321.7			−174.8[h]	−177.5	−196	−190 ± 25
1,2,3,4,7,8-HxCDD		−196.6		−382.2			−178.8[h]	−197.0	−215	−220 ± 30
1,2,3,4,6,7,8-HpCDD		−200.8		−401.5			−183.5[h]	−216.5	−236	−246 ± 35
OCDD		−203.5		−419.2			−188.5	−236.0	−255	−275 ± 40
				Dibenzofuran and Polychlorinated Dibenzofurans						
DF	55.3 ± 0.3[d] 47.3 ± 4.8[e]			83.3[f]			55.2[i]	55.2[i]	55.3[i]	55.3 ± 0.3[i]
1-CDF				26.0			26.6[h]	25.7	25	25 ± 5
2,3-DCDF				−15.0			5.8[h]	3.7	3	3 ± 5
2,3,7,8-TCDF		−37.2		−113.3			−52.1[h]	−47.8	−50	−50 ± 10
1,2,3,6,7-PnCDF		−42.3		−112.9		−191.3 [g]	−56.1[h]	−67.3	−71	−76 ± 20
1,2,3,4,7,8-HxCDF		−54.8		−149.7			−58.7[h]	−86.8	−90	−105 ± 25
1,2,3,4,6,7,8-HpCDF		−63.0		−140.1			−63.1[h]	−106.3	−111	−132 ± 30
OCDF		−50.5		−182.8			−63.7	−125.8	−130	−161 ± 35

[a] Kolesov et al. (1995); Lukyanova et al. (1997). [b] Kolesov et al. (1996). [c] Papina et al. (1996). [d] Chirico et al. (1990). [e] Sabbah (1991). [f] Adopted from Cox and Pilcher (1970); the same value is recommended by Pedley (1994). [g] 1,2,4,7,8-PnCDF. [h] Values are given for appropriate isomer group. [i] Experimental value by Chirico et al. (1990). [j] Experimental value by Lukyanova et al. (1997).

enthalpy of formation values have been estimated on the assumption that the difference between the value for any PCDD (or PCDF) and dibenzo-*p*-dioxin (or dibenzofuran) is the same as the difference between suitable chlorinated benzene(s) and benzene. The chlorination of each ring in PCDDs and PCDFs is considered to have no influence on the other benzene ring. As an example, the derivation of enthalpy of formation of 2,3,7,8-TCDD and 1,2,6,8-TCDF (in kJ·mol^{-1}) is shown as follows:



The $\Delta_f H°$(298.15 K) values for DD and DF are the experimental ones (Lukyanova et al., 1997; Chirico et al., 1990); the values of the enthalpy of formation for benzene and chlorinated benzenes were taken from the compilation by Pedley (1994).

In our previous work (Dorofeeva and Gurvich, 1996), we used the estimated value of the enthalpy of formation of DD (Table 1) and the $\Delta_f H°$(298.15 K) values for benzene and chlorinated benzenes from a previous compilation by Pedley et al. (1986). Data for the tri- and tetrachlorobenzenes were missing in the compilation of Pedley et al. (1986), and these were taken from TRC Tables (TRC, w-7330, 1984) (Table 2) where their values were estimated by empirical correlation. In this work, the enthalpies of formation of 1,2,3-, and 1,2,4-trichlorobenzene and 1,2,3,4-tetrachlorobenzene, required to estimate the $\Delta_f H°$(298.15 K) values of PCDDs and PCDFs, were taken from experimental data of Platonov and Simulin (1983, 1985) recommended in the new compilation of Pedley (1994). Because of appreciable difference between values of the enthalpy of formation adopted here and earlier (Dorofeeva and Gurvich, 1996) for the three above compounds, the new estimated enthalpy of formation values are quite different from those estimated in the work of Dorofeeva and Gurvich (1996) for PCDDs and PCDFs with 1,2,3-, 1,2,4-, and 1,2,3,4- chlorine substitution of benzene rings (Table 1).

To estimate the gas-phase enthalpies of formation of PCDDs and PCDFs, Thompson (1995) developed a group contribution method based on the experimental data for chlorinated benzenes, quinones, hydroquinones, and phenols. Pointing at often considerable uncertainties of the experimental enthalpies of formation for chlorinated organic compounds, Thompson (1995) excluded the experimental data of Platonov and Simulin (1983, 1984, 1985) from consideration. At the same time Thompson (1995) included the value of $\Delta_f H°$(298.15 K) for hexachlorobenzene recommended by Pedley (1994) (Table 2), although this value would not seem quite accurate and possibly was overestimated. The different attitudes to the experimental data of Platonov and Simulin (1983, 1984, 1985) is the main reason for discrepancies in enthalpy of formation values estimated in this work and by Thompson (1995) for PCDDs and PCDFs with the high degrees of chlorination. We believe that to resolve the contradictions in these two models, reliable experimental data should be determined for chlorinated benzenes and for any of the tri- and more chlorinated dibenzo-*p*-dioxins or dibenzofurans.

Entropies and Heat Capacities of Gaseous Compounds

The values of the ideal gas entropy derived from calorimetric measurements are known for unsubstituted dibenzofuran only (Chirico et al., 1990). For DD, PCDDs, and PCDFs, the $S°(T)$ and $C_p°(T)$ values were estimated by a group additivity approach and by statistical thermodynamics method (Shaub, 1982b; Rordorf, 1989; Murabayashi and Moesta, 1992; Thompson, 1994b, 1995; Dorofeeva and Gurvich, 1996). In our previous work (Dorofeeva and

Table 2. Enthalpies of Formation for Gaseous Benzene and Its Chlorinated Derivatives[a]

molecule	$\Delta_f H°(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}})$: compilation of exptl data by Pedley et al. (1986)	values recommended by TRC (1984)[b]	exptl data: Platonov and Simulin (1983, 1984, 1985)	exptl data: Platonov et al. (1985)	compilation of exptl data by Pedley (1994)
benzene	82.6 ± 0.7				*82.6 ± 0.7*
chlorobenzene	52.0 ± 1.3	51.1	54.4	54.3 ± 1.3	*52.0 ± 1.3*
1,2-dichlorobenzene	30.2 ± 2.1	29.7	33.0	33.9 ± 3.1	*30.2 ± 2.1*
1,3-dichlorobenzene	25.7 ± 2.1	25.5	28.1	29.5 ± 1.8	*25.7 ± 2.1*
1,4-dichlorobenzene	22.5 ± 1.5	22.2	24.6	25.7 ± 1.3	*22.5 ± 1.5*
1,2,3-trichlorobenzene		[9.0]	3.8	−1.7 ± 2.2	*3.8 ± 0.7*
1,2,4-trichlorobenzene		[−0.2]	−8.1	−8.8 ± 1.8	*−8.1 ± 1.0*
1,3,5-trichlorobenzene		[−6.9]	−13.4	−13.0 ± 3.6	−13.4 ± 1.0
1,2,3,4-tetrachlorobenzene		[−9.6]	−25.4	−26.8 ± 3.5	*−25.4 ± 1.0*
1,2,3,5-tetrachlorobenzene		[−20.1]	−34.9	−35.3 ± 3.7	−34.9 ± 1.0
1,2,4,5-tetrachlorobenzene		[−23.4]	−32.6	−37.5 ± 3.0	−32.6 ± 0.8
pentachlorobenzene		[−29.1]		−40.0 ± 8.7	−40.0 ± 8.7
hexachlorobenzene	−35.5 ± 9.4	−33.9	−44.7	−56.2 ± 8.5	−35.5 ± 9.3

[a] Values of $\Delta_f H°(298.15\ \mathrm{K})$ accepted in this work for estimating the enthalpies of formation of PCDDs and PCDFs are italicized. [b] Experimental data for mono-, di-, and hexachlorobenzenes were taken from Cox and Pilcher (1970) and Stull et al. (1969). Data for tri-, tetra-, and pentachlorobenzenes given in square brackets were estimated by empirical correlation.

Gurvich, 1996), the procedure for estimating the values of gas-phase thermodynamic functions for PCDDs and PCDFs has been developed from evaluated values of molecular parameters. In the present work, we have revised the estimate of vibrational frequencies on the basis of recent theoretical investigation of vibrational spectra of four tetrachlorinated dibenzo-*p*-dioxins (TCDDs) by Rauhut and Pulay (1995).

To calculate the entropy and heat capacity values by statistical thermodynamics method, it is necessary to know the structural parameters and the vibrational frequencies of the molecule. On the basis of X-ray diffraction and theoretical data for DD, DF, and some of the PCDDs and PCDFs (Fokin et al., 1989; Sommer et al., 1997; Tai et al., 1989; Reppart et al., 1984; Cantrell et al., 1989; Boer et al., 1973; Rissanen et al., 1987; Koester et al., 1988; Hileman et al., 1989; Kao et al., 1985; Reddy et al., 1989), the following structural parameters for planar geometry were estimated in this work:

for PCDDs

$$r(\mathrm{C{-}C}) = 139.5\ \mathrm{pm},\quad r(\mathrm{C{-}O}) = 138\ \mathrm{pm},\quad r(\mathrm{C{-}H}) = 108\ \mathrm{pm},\quad r(\mathrm{C{-}Cl}) = 173\ \mathrm{pm}$$

$$\angle\mathrm{C{-}C{-}C} = \angle\mathrm{C{-}C{-}H} = \angle\mathrm{C{-}C{-}Cl} = 120°,\quad \angle\mathrm{C{-}O{-}C} = 116°,\quad \angle\mathrm{C{-}C{-}O} = 122°$$

for PCDFs

$$r(\mathrm{C{-}C}) = 140\ \mathrm{pm},\quad r(\mathrm{C{-}O}) = 138\ \mathrm{pm},\quad r(\mathrm{C{-}H}) = 108\ \mathrm{pm},\quad r(\mathrm{C{-}Cl}) = 173\ \mathrm{pm}$$

$$\angle\mathrm{C{-}O{-}C} = 106°,\quad \angle\mathrm{C{-}C{-}O} = 111.37°,\quad \angle\mathrm{C{-}C{-}C} = 105.63°\ \text{(furan ring)},\quad \angle\mathrm{C{-}C{-}C} = 117.5°\ \text{and}\ 121.25°\ \text{(benzene ring)}$$

(H and Cl atoms are in the lines bisecting the corresponding C−C−C angles).

Vibrational frequencies of DF have been assigned from infrared and Raman spectra of crystals and solution and normal coordinate calculations (Bree et al., 1973; Danchinov et al., 1981, 1985; Gastilovich et al., 1984). The infrared spectra of a number of PCDDs have been measured in the gas phase and in rare gas matrices, and incomplete vibrational assignments have been reported (Sommer et al., 1997; Gurka et al., 1985, 1986; Wurrey et al., 1986; Grainger and Gelbaum, 1987; Grainger et al., 1988a,b, 1989; Grainger, 1989). Rauhut and Pulay (1995) have calculated the vibrational spectra of four TCDDs by scaled quantum mechanical method. Values of fundamental vibrations obtained by these authors reproduce the experimental infrared spectra well and predict the unobserved frequencies. Available vibrational assignments for DF and PCDDs, as well as for chlorinated benzenes, anthracene, 1,4-dioxin, and furan, were used in this work to develop the simplified force field approximation for PCDDs and PCDFs. Earlier the same procedure was successfully used for estimating the thermodynamic functions of polycyclic aromatic hydrocarbons (Dorofeeva et al., 1986a; Dorofeeva and Gurvich, 1988a, 1989; Moiseeva et al., 1989; Moiseeva and Dorofeeva, 1990). The distinguishing feature of the proposed method is that the force constants are calculated to best fit not only the vibrational frequencies but also the experimental data on entropy or heat capacity if the latter are known in the literature. It has been shown (Dorofeeva et al., 1986a; Dorofeeva and Gurvich, 1988a, 1989; Moiseeva et al., 1989; Moiseeva and Dorofeeva, 1990) that a simple force field is suitable for the evaluation of vibrational contribution to the thermodynamic functions: the difference in experimental and calculated entropy values was within the limits of the experimental accuracy for naphthalene, anthracene, phenanthrene, pyrene, acenaphthene, and fluorene. In the present work we have extended this approach to PCDDs and PCDFs. For the set of internal coordinates arising from C and H atoms, the force constants were transferred from polycyclic aromatic hydrocarbons (Dorofeeva et al., 1986a; Dorofeeva and Gurvich, 1989). The remaining force constants were obtained by a least-squares refinement to provide a satisfactory fit to known fundamentals of DF, PCDDs, and chlorinated benzenes and to the experimental values of the entropy of DF and to a preliminary estimate of the entropy of DD (see below). Final simplified valence force constants are listed in Table 3. Twenty-six force constants from this table were used to calculate the vibrational frequencies of DD, DF, and all isomers of PCDDs and PCDFs.

The observed and calculated frequencies for DF are given in Table 4. The entropy values calculated by using these two assignments are listed in Table 5 together with the experimental data. As seen from Table 5, the difference between the experimental entropies and those calculated from vibrational frequencies is outside the range of experi-

Table 3. Valence Force Constants for PCDDs and PCDFs

	force constant type	DD and PCDDs	DF and PCDFs
1	C−C (benzene ring)[a]	6.42	
2	C−C (furan ring)[a]	−	5.15
3	C−O[a]	6.00	
4	C−H[a]	5.06	
5	C−Cl[a]	3.58	
6	CCC (benzene ring)[b]	0.90	
7	CCC (furan ring)[b]	−	1.19
8	CCO[b]	1.19	
9	COC[b]	1.31	
10	CCH[b]	0.48	
11	CCCl[b]	1.04	
12	CC,CC = CC,CO = CO,CO[a]	0.33	
13	CC, CCl[c]	1.90	
14	CC,CCC = CC,CCO = CO,COC = CO,CCO[c]	0.30	
15	CC,CCH[c]	0.34	
16	CC,CCCl[c]	0.71	
17	CCl, CCCl[c]	0.43	
18	wag CH[b]	0.22	
19	wag CC[b]	0.37	
20	wag CCl[b]	0.35	
21	tors (HC−CH)[b]	0.31	
22	tors (HC−CC) = tors (HC−CO)[b]	0.40	
23	tors (CC−CC) = tors (CC−CO)[b]	0.23	0.004
24	tors (HC−CCl) = tors (OC−CCl)[b]	0.31	
25	tors (ClC−CCl)[b]	0.50	
26	tors (C−O)[b]	0.13	1.00

[a] 10^2 N/m. [b] 10^{-18} N/m. [c] 10^{-8} N/m.

Table 4. Comparison of the Experimental Vibrational Assignment for Dibenzofuran with Fundamental Frequencies Calculated in This Work

assignmt	ν_{exp}[a]/cm^{-1}	ν_{calc}/cm^{-1}	assignmt	ν_{exp}[a]/cm^{-1}	ν_{calc}/cm^{-1}	assignmt	ν_{exp}[a]/cm^{-1}	ν_{calc}/cm^{-1}
A_1 1	3085	3053	20	220	244	B_2 39	3090	3053
2	3066	3053	A_2 21	*984*	1010	40	3069	3053
3	3048	3051	22	*947*	970	41	3058	3051
4	3016	3050	23	*862*	888	42	3045	3050
5	1633	1598	24	768	796	43	1599	1620
6	1599	1581	25	*726*	705	44	1589	1564
7	1488	1509	26	*552*	580	45	1471	1499
8	1447	1442	27	*405*	458	46	1451	1416
9	1346	1389	28	293	289	47	1324	1385
10	1308	1288	29	*130*	118	48	1282	1305
11	1273	1260	B_1 30	973	1007	49	1193	1246
12	1242	1207	31	930	948	50	1153	1172
13	1147	1171	32	881	832	51	1116	1124
14	1102	1106	33	783	753	52	1022	1048
15	1008	1011	34	722	675	53	999	986
16	850	822	35	566	518	54	840	842
17	755	737	36	446	430	55	616	618
18	660	623	37	318	322	56	554	596
19	420	406	38	130	138	57	517	499

[a] These vibrational frequencies were obtained by Danchinov et al. (1981, 1985) and Gastilovich et al. (1984) on the basis of the experimental study of the infrared spectrum of crystalline dibenzofuran, the normal coordinate calculations, and the partial vibrational assignment of Bree et al. (1973) from Raman spectra of dibenzofuran crystals and solution. Experimentally unobserved frequencies given in italics are calculated by Gastilovich et al. (1984).

Table 5. Comparison of the Experimental Ideal Gas Entropies for Dibenzofuran with Values Calculated by Statistical Thermodynamics Method

	$S°/(J \cdot K^{-1} \cdot mol^{-1})$				
		calc by statistical thermodynamics method			
	expt Chirico et al. (1990)	exptl vibrational freq from Table 4		calcd vibrational freq from Table 4	
T/K		$S°$	Δ[d]	$S°$	Δ[d]
298.15	374.4 ± 0.6[a,b]	376.1	−1.7	375.9	−1.5
300	375.5 ± 0.6[a,b]	377.1	−1.6	376.9	−1.4
	375.8[c]		*−1.3*		*−1.1*
320	387.0 ± 0.4[a,b]	388.1	−1.1	387.9	−0.9
340	398.3 ± 0.3[a,b]	399.2	−0.9	398.9	−0.6
360	409.7 ± 0.3	410.3	−0.6	410.0	−0.3
380	421.0 ± 0.3	421.3	−0.3	421.1	−0.1
400	432.2 ± 0.3	432.4	−0.2	432.1	0.1
420	443.4 ± 0.3	443.5	−0.1	443.1	0.3
440	454.5 ± 0.3	454.4	0.1	454.1	0.4
460	465.5 ± 0.3	465.4	0.1	465.0	0.5
480	476.5 ± 0.4	476.2	0.3	475.9	0.6
500	487.4 ± 0.4	487.0	0.4	486.6	0.8
520	498.2 ± 0.5	497.7	0.5	497.2	1.0
540	508.9 ± 0.5	508.2	0.7	507.8	1.1
560	519.5 ± 0.7	518.7	0.8	518.2	1.3
580	530.0 ± 0.7	529.0	1.0	528.6	1.4
600	540.4 ± 0.9	539.3	1.1	538.8	1.6
620	550.8 ± 1.1[a]	549.4	1.4	548.9	1.9
640	561.1 ± 1.2[a]	559.4	1.7	558.9	2.2
660	571.3 ± 1.4[a]	569.3	2.0	568.7	2.6
680	581.5 ± 1.6[a]	579.0	2.5	578.5	3.0
700	591.6 ± 1.7[a]	588.6	3.0	588.1	3.5
	590.3[c]		*1.7*		*2.2*
720	601.6 ± 1.9[a]	598.1	3.5	597.6	4.0

[a] Values at this temperature were calculated with extrapolated vapor pressures calculated from the fitted Cox coefficients. [b] Values at this temperature were calculated with graphically extrapolated values of the liquid-phase heat capacities. [c] Revised values (Steele, 1995); see text. [d] $\Delta = S°_{exp} - S°_{calc}$.

mental error excepting the values for 320 K < T < 420 K. Chirico et al. (1990) pointed out the relatively large deviations between experimental and calculated entropy values at low temperatures and suggested that one or more fundamental vibrational modes were assigned too low. However, our attempts to reduce this difference by refining the force constants were not successful: the discrepancies can be reduced in either the low-temperature region or the high-temperature region, but not both simultaneously. Although the expected overall errors of calculated entropy values should be practically within the range of deviation between experimental and calculated $S°(T)$ values, it is difficult to understand the trend of these differences except to propose the underestimation of error limits of experimental entropy values or incorrect vibrational assignment (not only for low-frequency modes) for DF.

As our calculations were being completed, the papers concerning new studies of vibrational spectra (Klots and Collier, 1996) and modified calorimetric data (Steele, 1995) for DF became known. The original calorimetric entropy values (Chirico et al., 1990) were updated by inclusion of the third virial coefficient. Steele (1995) reported the modified entropy values $S°_{exp}$ (300 K) = 375.8 J·K^{-1}·mol^{-1} and $S°_{exp}$ (700 K) = 590.3 J·K^{-1}·mol^{-1}. For these values, the differences between calorimetric and calculated values become slightly smaller. Klots and Collier (1996) proposed the new assignment of fundamentals for DF based on the gas-, liquid-, and solid-phase vibrational spectra and scaled AM1 force field calculation. Their assignment supports the majority of fundamentals previously assigned, although several previous ambiguities are removed. From the assigned fundamentals, the following entropy values were calculated: $S°$(300 K) = 377.7 J·K^{-1}·mol^{-1} and $S°$(700 K) = 588.9 J·K^{-1}·mol^{-1}. Klots and Collier consider that these values compare extremely well with those from calorimetry, the difference in entropy values being well within the combined uncertainties of the calorimetric and statistical mechanics methods. Since our calculated entropy values are practically in agreement with calorimetric values such as those calculated by Klots and Collier (1996), we did not recalculate the thermodynamic functions for DF and PCDFs.

Table 6. Entropy Values for Gaseous DD, DF, and Some of the PCDDs and PCDFs

	$S°(298.15\ K)/(J{\cdot}K^{-1}{\cdot}mol^{-1})$							
		group additivity approach			calc by statistical thermodynamics method			
molecule	exp Chirico et al. (1990)	Ritter and Bozzeli (1994)	Thompson (1994b)	Thompson (1995)	Shaub (1982)	Murabayashi and Moesta (1992)	Dorofeeva and Gurvich (1996)	this work
			Dibenzo-*p*-dioxin and Polychlorinated Dibenzo-*p*-dioxins					
DD			295.8	388[b]	387.8		386.6	396.5
1-CDD			343.8[a]	410.6	420.9		422.5	437.4
2,3,7,8-TCDD		516.9	440.6[a]	478.4	478.1	488.6	495.1	510.4
OCDD			484.5	568.8	572.1		601.2	624.1
			Dibenzofuran and Polychlorinated Dibenzofurans					
DF	374.4 ± 0.6		402.2	374.4[c]			375.9	375.9
1-CDF			459.7[a]	397.0			408.4	411.7
1,2,6,7-TCDF			540.9[a]	464.8			491.4	496.5
1,2,4,7,8-PnCDF		565.5	560.8[a]	487.4			518.9	525.7
OCDF			591.1	555.2			592.2	603.7

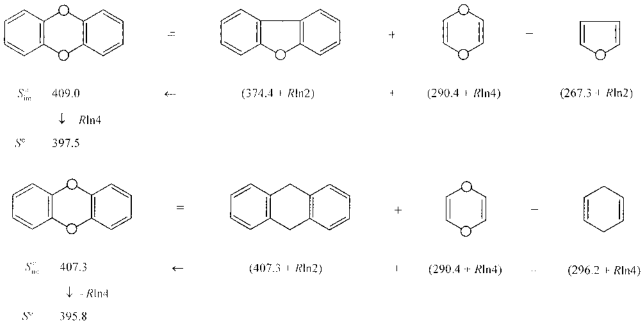
[a] Values are given for appropriate isomer group. [b] Adopted due to Shaub (1982b). [c] Experimental value by Chirico et al. (1990).

Table 7. Heat Capacity Values for Gaseous DD, DF, and Some of the PCDDs and PCDFs

	$C_p°/(J{\cdot}K^{-1}{\cdot}mol^{-1})$					
	group additivity approach			calc by statistical thermodynamics method		
molecule	Rordorf (1989)	Ritter and Bozzelli (1994)	Thompson (1994b)	Shaub (1982b)	Dorofeeva and Gurvic (1996)	this work
			Dibenzo-*p*-dioxin and Polychlorinated Dibenzo-*p*-dioxins			
DD	182.8		206.0	176.3	176.9	180.2
1-CDD	200.2[a]		223.4[a]	191.0	189.8	195.9
2,3,7,8-TCDD	252.4[a]	246.7	279.6[a]	237.6	234.0	241.2
OCDD	322.0		312.9	296.9	296.1	305.8
			Dibenzofuran and Polychlorinated Dibenzofurans			
DF	173.5		185.2		163.5	163.5
1-CDF	190.9[a]		201.8[a]		177.5	179.4
1,2,6,7-TCDF	243.1[a]		257.3[a]		223.4	225.9
1,2,4,7,8-PnCDF	260.5[a]	229.0	273.2[a]		236.1	241.1
OCDF	312.7		309.7		284.0	289.7

[a] Values are given for appropriate isomer group.

The entropy and heat capacity values for DD, DF, and some of the PCDDs and PCDFs calculated in this work using the estimated molecular constants are given in Tables 6 and 7. From these tables, it may be seen that the most significant difference with $S°$ values estimated before occurs for PCDDs. So our calculated value of entropy for 2,3,7,8-TCDD (510.4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) is 32 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ larger than that obtained by Shaub (1982b) from estimated molecular parameters. This difference is due to essentially lower values accepted in this work for low-frequency modes, including the large-amplitude butterfly vibration. It should be noted that an even larger value of entropy of 2,3,7,8-TCDD (517.4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) is obtained when vibrational frequencies are taken directly from theoretical calculation (Rauhut and Pulay, 1995). Recently Sommer et al. (1997) investigated some of the PCDDs and PCDFs by FT-IR spectroscopy. For assignment of vibrations, some IR spectra were simulated by ab initio calculations. $S°(T)$ values of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1,2,3,4,6,7,8-HpCDD) calculated for vibrational assignment of Sommer et al. (1997) are 7−13 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ lower than values obtained in this work, whereas $S°(T)$ values of 1,2,3,4,6,7,8-HpCDF are 3−11 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ larger than our values. To find the transferable force field for PCDDs, we adjusted the force constants (Table 3) not only to theoretical vibrational assignments of chlorinated benzenes and four TCDDs (Rauhut and Pulay, 1995) but also to the value of $S°(DD, g, 298.15\ K) \approx 397\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ estimated by the difference method:



($S°_{int} = S° + R \ln \sigma$, where σ is the symmetry number; the $S°(T)$ values for the structurally similar molecules were taken from Chirico et al. (1990), Dorofeeva (1992a,b), Dorofeeva and Gurvich (1988b), and Dorofeeva et al. (1986b). The relationships mentioned above show that the difference method can be used not only to predict unmeasured properties but also to provide a double-check on the reasonableness of published experimental and theoretical data.

Using the structural parameters and vibrational frequencies estimated as described above, the thermodynamic functions of 75 possible isomers of PCDDs and 135 of PCDFs were calculated in this work by the rigid-rotor harmonic-oscillator approximation. The full tables of thermodynamic functions of DD, DF, PCDDs, and PCDFs can

Table 8. Group Additivity Values for DD, DF, PCDDs, and PCDFs

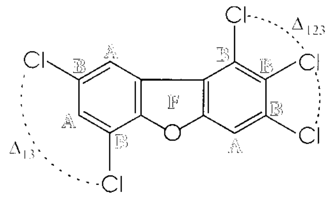
group	$\Delta_f H°$/(kJ·mol^{-1})	$H°$(298.15 K) − $H°$(0)/(kJ·mol^{-1})	$S°_{int}$(298.15 K)/(J·K^{-1}·mol^{-1})	$C_p°$/(J·K^{-1}·mol^{-1})								
				T = 298.15 K	T = 300 K	T = 400 K	T = 500 K	T = 600 K	T = 800 K	T = 1000 K	T = 1200 K	T = 1400 K	T = 1500 K
A	13.765	3.2568	48.327	21.032	21.170	28.188	34.028	38.685	45.383	49.858	52.985	55.237	56.128
B	−16.835	6.5248	77.662	36.422	36.556	42.891	47.620	51.115	55.636	58.229	59.810	60.831	61.208
D	−169.32	2.1373	20.764	11.788	11.825	13.556	14.882	15.909	17.326	18.202	18.770	19.155	19.302
F	−54.823	−0.91461	−5.0154	−4.6059	−4.6090	−4.6710	−4.6765	−4.6841	−4.6981	−4.6912	−4.6709	−4.6470	−4.6349
Δ_{12}	8.8	0.03666	−1.3300	0.10790	0.10581	0.026337	0.0090665	−0.022808	−0.026440	−0.022413	−0.018044	−0.01444	−0.012981
Δ_{13}	4.3	0.092512	−0.012373	0.17136	0.16809	0.062259	.027975	0.015630	0.0080352	0.0053498	0.0039564	0.0029721	0.0026854
Δ_{14}	1.1	0.25399	0.50427	0.75425	0.74864	0.50288	0.35128	0.25802	0.15688	0.10617	0.076696	0.05805	0.051180
Δ_{123}	13.0	0.21565	−2.4838	0.51584	0.50735	0.19421	0.058268	0.0007798	−0.031310	−0.032610	−0.028221	−0.02356	−0.021351
Δ_{124}	1.1	0.34388	−1.0075	0.92063	0.91052	0.50851	0.30360	0.19578	0.098823	0.059467	0.039951	0.02854	0.024892
Δ_{1234}	14.4	0.52376	−3.4338	1.4004	1.3818	0.67353	0.33468	0.17140	0.046691	0.010275	−0.0016937	−0.005727	−0.0061494

[a] $S°_{int}$(298.15 K) = $S°$(298.15 K) + R ln σ, where σ is the symmetry number.

be obtained from an updated database IDEALGAS created by the Thermocenter of the Russian Academy of Science and the Thermodynamics Research Center (TRC) of Texas A&M University (Gurvich et al., 1992).

Group Additivity Scheme for Estimating the Thermodynamic Properties of Gaseous DD, DF, PCDDs, and PCDFs

To approximate the thermodynamic properties estimated in this work, we develop the group additivity scheme with 10 parameters (Table 8). According to the designation by Benson (1976), groups A and B can be written as $C_B-(H)$ and $C_B-(Cl)$, respectively. Group D consists of two $O-(C_B)_2$ and four $C_B-(C_B)_2(O)$ groups and describes the dioxin frame taken as a whole. Similarly group F describes the furan frame. Six Δ corrections are applied for 1,2-, 1,3-, 1,4-, 1,2,3-, 1,2,4- and 1,2,3,4-interactions of chlorine atoms. For example, the equation for calculating the thermodynamic properties of 1,2,3,6,8-PnCDF contains the following groups:



$3A + 5B + F + \Delta_{13} - \Delta_{123}$

The average difference between $S°$(298.15 K), $C_p°$(298.15 K), and $H°$(298.15 K) − $H°$(0) values obtained by the group additivity approach and calculated from molecular constants are 0.3 J·K^{-1}·mol^{-1}, 0.4 J·K^{-1}·mol^{-1}, and 0.1 kJ·mol^{-1}, respectively (the appropriate maximum deviations are 1.4 J·K^{-1}·mol^{-1}, 1.1 J·K^{-1}·mol^{-1}, and 0.3 kJ·mol^{-1}).

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Received for review October 5, 1998. Accepted January 21, 1999. This work was supported by the International Science Foundation and the Government of Russian Federation (Grants No. M8Z000 and M8Z300) and by the Russian Foundation for Basic Research (Grants No. 94-02-05208 and 96-02-16223).

JE980238R