Thermochemical Properties of Polychlorinated Biphenylenes

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Calculation of thermodynamic properties of polychlorinated biphenylenes in the ideal gas state using the spectral data and molecular parameters, obtained from quantum chemical calculations, was carried out in the temperature region from 250 K to 2000 K. Relative stabilities of isomeric polychlorinated biphenylenes were calculated.

Introduction

Although polychlorinated biphenylenes do not belong to the most often-mentioned pollutants, toxicity of biphenylene and its chlorinated derivates was reported.[1,2] On the other hand, polychlorinated biphenylenes can convert to polychlorinated dibenzodioxins by means of oxidation. In comparison to polychlorinated biphenyls and dibenzodioxins, whose thermodynamic properties were thoroughly studied, thermochemical data are available only for nonsubstituted biphenylene. The aim of this work is calculation of thermochemical properties of the complete series of polychlorinated biphenylenes. Labeling of atoms in the biphenylene molecule is denoted in Figure 1.

Molecular and Thermochemical Data of Biphenylene

The molecular structure of the biphenylene molecule was determined by Fawcett and Trotter[3] by X-ray measurements in the solid state and by Yokozecki et al.[4] using electron diffraction in the gaseous state.

Vibration spectra of biphenylene were measured by Pecile and Lunelli[5] in the solid and gaseous states. Later, Whitmer et al.[6] and Kautz et al.[7] reported new measurements of the vibration spectra as well as the assignment of molecular vibrations. On the other hand, a complete vibration assignment from the experimental data was not done yet, and frequencies of some vibration modes were calculated by means of the force field method or by means of quantum chemical calculations in the mentioned works.

Good[8] measured the enthalpy of combustion of biphenylene. His measurements led to the value 333.4 kJ·mol^{-1} for enthalpy of formation of solid biphenylene at 298.15 K. The older work by Bedfor et al.[9] gave 353.1 kJ·mol^{-1}. The value of enthalpy of sublimation of biphenylene (87.3 kJ·mol^{-1}) was determined by Osborn and Scott[10] from the temperature dependence of the saturated vapor pressure. Morawetz[11] reported a value of 83.8 kJ·mol^{-1}, obtained from the direct calorimetric measurements. The combination of the values of Good and Morawetz leads to the value 417.18 kJ·mol^{-1} for enthalpy of formation of gaseous biphenylene. This value is in agreement with those reported in the tables by Frenkel et al.[12] and was used in this work.

Thermochemical properties of biphenylene in the ideal gas state are listed in the tables by Frenkel et al.[12] Nevertheless, these data were calculated on the basis of the vibration frequencies and included both experimental and calculated values.

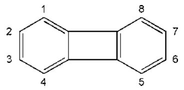

Figure 1. Labeling of atoms in the biphenylene molecule.

Method of Computation

The molecules of polychlorinated biphenylenes were studied by means of the density functional theory. Becke's three-parameter functional (B3LYP)[13] and the 6-31G** basis set[14] were used for the calculations. The calculations were carried out with the Gaussian 03W computer program.[15]

For all the molecules studied, the calculations were done in three steps. The first step included a preliminary optimization of the molecular geometry, using the Hartree–Fock calculation and the standard STO-3G basis set. The second step was a refinement of the molecular geometry, using the B3LYP method and the 6-31G** basis set. The molecular vibrations and the zero-point energy were calculated in the last step. This step was carried out using the same method and basis and the molecular geometry, optimized in the second step.

These calculations yielded the values of rotational constants, vibration frequencies, and the sum of electronic and thermal enthalpies, which were used for calculations of thermochemical properties. The sum of electronic and thermal enthalpies represents a sum of the molecular energy and the zero-point energy, recalculated from absolute zero to the temperature 298 K.

Peck et al.[16] calculated the enthalpy of formation of biphenylene, using the ab initio calculations. These results were corrected by means of the aromatic group equivalents, obtained from the experimental enthalpies of formation of the similar compounds, using the least-squares method. Schulman and Disch[17] determined the enthalpy of formation of biphenylene, using the ab initio calculations and a homodesmic reaction

$$\text{acenapthylene} = \text{biphenylene}$$

The last method gave the better result.

The calculations of the enthalpies of formation by means of the ab initio calculation and an appropriate homodesmic reaction were done for polychlorinated biphenyls by Dorofeeva et al.,[18]

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Table 1. Experimental r and Calculated r_{calcd} Interatomic Distances in the Biphenylene Molecule[a]

bond	r / nm	ref	r_{calcd} / nm
C_1–C_2	0.1428	3	0.142
	0.1421	4	
C_2–C_3	0.137	3	0.1389
	0.1371	4	
C_9–C_{10}	0.1524	3	0.1508
	>0.154	4	
C–H	0.1096	3	0.1086
	0.108	4	

[a] Labeling of atoms is in Figure 1.

Table 2. Comparison of the Tabulated[12] C°_{pm} and Calculated C°_{pm}(calcd) Values of Molar Heat Capacity of Biphenylene

T / K	C°_{pm} / $J\cdot K^{-1}\cdot mol^{-1}$	C°_{pm}(calcd) / $J\cdot K^{-1}\cdot mol^{-1}$
298.15	159.3	154.1
300	160.3	155.4
400	212.3	206.8
500	255.7	250.9
600	290.4	285.6
700	318.0	313.8
800	340.4	336.5
900	358.8	355.2
1000	374.0	370.9
1100	386.9	384.0
1200	398.0	395.2
1300	407.0	404.7
1400	415.0	412.9
1500	422.0	420.0

polychlorinated dibenzo-*p*-dioxins by Wang et al.,[19] and polybrominated dibenzo-*p*-dioxins and dibenzofurans by Li et al.[20]

For determination of the values of enthalpy of formation of polychlorinated biphenylenes, the following homodesmic reaction of biphenylene and chlorobenzene was used

$$C_{12}H_8 + nC_6H_5Cl = C_{12}H_{8-n}Cl_n + nC_6H_6$$

This reaction matches the requirements for reliable calculation of the enthalpy of formation because there is a similarity of bonding environment in the reactants and products and the values of the enthalpy of formation of used compounds were determined experimentally by means of combustion calorimetry.

The reaction enthalpy of the appropriate reaction was calculated as a difference between the sums of electronic and thermal enthalpies of the product and reactants. The values of enthalpy of formation were calculated from the Hess law. The values of enthalpies of formation of benzene and chlorobenzene were taken from the tables by Frenkel et al.[12]

The values of entropy, Gibbs energy, and molar heat capacity in the ideal gas state were calculated using the standard method of statistical thermodynamics in the approximation of the rigid rotator and harmonic oscillator. Entropies of elements, needed for calculation of Gibbs energies of formation, were taken from the tables by Chase et al.[21]

Results and Discussion

The interatomic distances in biphenylene, calculated by the geometry optimization, were compared with the experimental values. The comparison is listed in Table 1. The mean deviation between the calculated and experimental values is about 1 %, and the highest deviation is 2.1 %. Thus the accuracy of the optimization procedure described above can be considered as satisfactory.

Table 3. Comparison of the Experimental $\Delta_f H^\circ$ and Calculated $\Delta_f H^\circ$(calcd) Values of Enthalpy of Formation at $T = 298$ K of Polychlorinated Biphenyls

compound	$\Delta_f H^\circ$ / $kJ\cdot mol^{-1}$	ref	$\Delta_f H^\circ$(calcd) / $kJ\cdot mol^{-1}$
2,2′-dichlorbiphenyl	136.9	22	122.3
4,4′-dichlorbiphenyl	127.2	22	120.5

Table 4. Comparison of the Tabulated[12] and Calculated Values of Thermochemical Values at $T = 298$ K and Equilibrium Composition (Mole Fractions) of Dichlorobenzenes

compound	1,2-dichlorobenzene	1,3-dichlorobenzene	1,4-dichlorobenzene
$\Delta_f H^\circ$(exptl)/ $kJ\cdot mol^{-1}$	29.7	25.5	22.2
$\Delta_f H^\circ$(calcd)/ $kJ\cdot mol^{-1}$	33.8	25.7	23.4
S°(exptl)/ $J\cdot K^{-1}\cdot mol^{-1}$	342.0	343.5	336.7
S°(calcd)/ $J\cdot K^{-1}\cdot mol^{-1}$	342.0	343.3	337.6
$\Delta_f G^\circ$(exptl)/ $kJ\cdot mol^{-1}$	82.5	78.0	77.4
$\Delta_f G^\circ$(calcd)/ $kJ\cdot mol^{-1}$	82.5	77.8	76.4
equilibrium composition from experimental data	0.052	0.344	0.605
equilibrium composition from calculated data	0.014	0.435	0.551

The reliability of the calculations of the molecular vibration frequencies can be estimated with the help of comparison of the values of entropy and molar heat capacity. Thus, the entropy at 298 K and the molar heat capacities in the temperature region from 200 K to 1500 K for biphenylene were calculated by the described procedure and compared with the values listed by Frenkel et al.[12] The calculated value of entropy at 298 K was 369.7 $J\cdot K^{-1}\cdot mol^{-1}$, and the tabulated value is 374.5 $J\cdot K^{-1}\cdot mol^{-1}$. The values of molar heat capacity are presented in Table 2.

Because values of enthalpy of formation were not measured for chlorinated biphenylenes, the calculation of the formation enthalpy of two polychlorinated biphenyls, namely, 2,2′-dichlorobiphenyl and 4,4′-dichlorobiphenyl, was used as a test of the accuracy of the calculations of the enthalpy of formation. The values of enthalpy of formation of these compounds were measured by Smith et al.[22] A similar homodesmic reaction was considered as an appropriate thermochemical cycle

$$C_{12}H_{10} + C_6H_5Cl = C_{12}H_9Cl + C_6H_6$$

The results of calculations are summarized in the Table 3. The deviation of the calculated and experimental values of enthalpy of formation is about 8 %.

As an additional test of the methodology used, thermochemical properties and the composition of the equlibrium mixture at 298 K were calculated for dichlorobenzenes. The enthalpies of formation were calculated from the following homodesmic reaction

$$2C_6H_5Cl = C_6H_4Cl_2 + C_6H_6$$

The results are listed in Table 4. It follows from this table that the calculated values are usable for thermochemical calculations. On the other hand, calculations of chemical equlibria require the thermochemical data with high accuracy. Therefore, the methodology used can yield only a qualitative estimation of the equlibrium composition.

Table 5. Calculated Thermochemical Properties of Polychlorinated Biphenylenes at T = 298 K and Constants of Equation 1 for Molar Heat Capacity

isomer	$\Delta_f H°$ $kJ \cdot mol^{-1}$	$\Delta_f G°$ $kJ \cdot mol^{-1}$	$S°$ $J \cdot K^{-1} \cdot mol^{-1}$	a $J \cdot K^{-1} \cdot mol^{-1}$	b $J \cdot K^{-2} \cdot mol^{-1}$	$c \cdot 10^4$ $J \cdot K^{-3} \cdot mol^{-1}$	$d \cdot 10^8$ $J \cdot K^{-4} \cdot mol^{-1}$
1-chloro	386.3	456.5	402.2	−20.14	0.76	−4.53	9.55
2-chloro	386.7	457.1	401.6	−20.10	0.76	−4.54	9.57
1,2-dichloro	369.5	444.8	431.1	−1.03	0.75	−4.52	9.63
1,3-dichloro	359.5	434.5	432.4	−0.29	0.75	−4.52	9.62
1,4-dichloro	358.9	435.5	426.7	−0.39	0.75	−4.51	9.59
1,5-dichloro	356.6	433.2	426.8	−0.65	0.75	−4.52	9.61
1,6-dichloro	357.0	431.9	432.6	−0.43	0.75	−4.53	9.64
1,7-dichloro	357.3	432.3	432.3	−0.53	0.747	−4.526	9.640
1,8-dichloro	361.2	438.1	426.1	−0.857	0.75	−4.52	9.62
2,3-dichloro	370.5	447.8	424.5	−0.96	0.75	−4.53	9.65
2,6-dichloro	357.4	434.2	426.3	−0.41	0.75	−4.54	9.67
2,7-dichloro	357.6	434.5	426.0	−0.48	0.75	−4.53	9.66
1,2,3-trichloro	356.3	436.9	459.6	18.28	0.74	−4.52	9.70
1,2,4-trichloro	344.7	424.8	461.5	18.90	0.73	−4.50	9.66
1,2,5-trichloro	340.7	420.7	461.6	18.45	0.74	−4.52	9.70
1,2,6-trichloro	341.0	421.2	461.0	18.50	0.74	−4.53	9.72
1,2,7-trichloro	341.4	421.5	461.2	18.50	0.74	−4.53	9.73
1,2,8-trichloro	345.6	425.9	460.6	18.17	0.74	−4.52	9.71
1,3,5-trichloro	331.1	410.8	462.9	19.22	0.73	−4.51	9.69
1,3,6-trichloro	331.4	411.2	462.7	19.35	0.73	−4.52	9.71
1,3,7-trichloro	331.5	411.3	462.4	19.24	0.74	−4.52	9.72
1,3,8-trichloro	335.3	415.0	462.5	19.08	0.73	−4.51	9.70
1,4,5-trichloro	334.8	414.5	462.7	18.98	0.73	−4.50	9.66
1,4,6-trichloro	331.0	410.6	463.3	19.32	0.73	−4.51	9.68
2,3,5-trichloro	342.0	422.2	461.0	18.59	0.74	−4.52	9.72
2,3,6-trichloro	342.3	422.6	460.7	18.64	0.74	−4.53	9.74
1,2,3,4-tetrachloro	344.0	431.6	482.6	37.50	0.72	−4.50	9.74
1,2,3,5-tetrachloro	328.6	413.9	490.2	37.72	0.72	−4.51	9.77
1,2,3,6-tetrachloro	328.8	414.7	488.1	37.77	0.72	−4.52	9.80
1,2,3,7-tetrachloro	329.0	414.4	489.7	37.76	0.72	−4.52	9.80
1,2,3,8-tetrachloro	333.1	418.8	489.0	37.42	0.72	−4.52	9.78
1,2,4,5-tetrachloro	321.2	406.2	491.4	38.18	0.72	−4.50	9.73
1,2,4,6-tetrachloro	317.5	402.4	491.8	38.39	0.72	−4.51	9.76
1,2,4,7-tetrachloro	317.7	402.6	491.5	38.38	0.72	−4.50	9.76
1,2,4,8-tetrachloro	321.9	406.8	491.3	38.13	0.72	−4.50	9.74
1,2,5,6-tetrachloro	325.1	412.2	484.4	37.355	0.724	−4.517	9.784
1,2,5,7-tetrachloro	316.0	400.8	491.7	38.22	0.72	−4.51	9.77
1,2,5,8-tetrachloro	320.0	404.9	491.3	38.22	0.72	−4.51	9.77
1,2,6,7-tetrachloro	326.8	412.1	490.0	37.59	0.72	−4.52	9.80
1,2,6,8-tetrachloro	320.3	405.4	490.7	37.91	0.72	−4.52	9.79
1,2,7,8-tetrachloro	330.7	418.1	483.2	37.04	0.73	−4.53	9.81
1,3,5,7-tetrachloro	306.4	392.7	487.0	38.85	0.72	−4.51	9.77
1,3,5,8-tetrachloro	310.1	394.6	493.0	38.75	0.72	−4.50	9.74
1,3,6,7-tetrachloro	317.1	402.2	491.1	38.31	0.72	−4.52	9.80
1,3,6,8-tetrachloro	310.4	396.8	486.5	38.73	0.72	−4.51	9.77
1,4,5,8-tetrachloro	314.0	402.2	480.5	38.36	0.72	−4.49	9.72
1,4,6,7-tetrachloro	316.8	403.4	485.7	38.19	0.72	−4.51	9.76
2,3,6,7-tetrachloro	327.8	416.8	477.7	37.62	0.73	−4.53	9.83
1,2,3,4,5-pentachloro	321.5	412.2	518.3	56.68	0.71	−4.50	9.82
1,2,3,4,6-pentachloro	317.4	407.9	518.7	56.99	0.71	−4.51	9.84
1,2,3,5,6-pentachloro	313.7	404.3	518.7	56.66	0.71	−4.51	9.86
1,2,3,5,7-pentachloro	304.5	394.7	519.9	57.35	0.71	−4.51	9.85
1,2,3,5,8-pentachloro	304.5	394.7	519.9	57.35	0.71	−4.51	9.85
1,2,3,6,7-pentachloro	308.5	398.8	519.5	57.09	0.71	−4.50	9.83
1,2,3,6,8-pentachloro	315.0	405.7	518.3	56.79	0.71	−4.52	9.88
1,2,3,7,8-pentachloro	308.7	399.1	519.5	57.20	0.71	−4.51	9.86
1,2,4,5,6-pentachloro	318.7	409.6	517.7	56.32	0.71	−4.52	9.88
1,2,4,5,7-pentachloro	306.8	396.9	520.2	57.1	0.71	−4.50	9.83
1,2,4,5,8-pentachloro	297.2	386.9	521.8	57.96	0.71	−4.493	9.81
1,2,4,6,7-pentachloro	301.5	391.4	521.0	57.58	0.71	−4.49	9.79
1,2,4,6,8-pentachloro	297.6	387.3	521.5	57.87	0.71	−4.50	9.82
1,2,4,7,8-pentachloro	307.6	397.8	519.9	57.05	0.71	−4.50	9.83
1,2,3,4,5,6-hexachloro	307.6	403.6	546.6	75.53	0.70	−4.51	9.92
1,2,3,4,5,7-hexachloro	297.8	393.3	548.3	76.36	0.70	−4.50	9.91
1,2,3,4,5,8-hexachloro	302.2	399.8	541.4	75.93	0.70	−4.49	9.89
1,2,3,4,6,7-hexachloro	304.1	401.7	541.4	75.94	0.70	−4.51	9.92
1,2,3,5,6,7-hexachloro	302.7	400.3	541.3	75.77	0.70	−4.51	9.94
1,2,3,5,6,8-hexachloro	295.9	391.3	548.6	76.32	0.70	−4.50	9.90
1,2,3,5,7,8-hexachloro	296.5	392.1	548.1	76.16	0.70	−4.50	9.91
1,2,3,6,7,8-hexachloro	307.5	405.4	540.1	75.44	0.70	−4.52	9.96
1,2,4,5,6,8-hexachloro	289.3	386.2	543.7	76.65	0.70	−4.49	9.88
1,2,4,5,7,8-hexachloro	289.6	386.5	543.5	76.59	0.70	−4.49	9.88
1,2,3,4,5,6,7-heptachloro	297.0	398.2	575.3	94.73	0.69	−4.51	10.00
1,2,3,4,5,6,8-heptachloro	290.5	391.5	576.0	95.04	0.69	−4.49	9.97
1,2,3,4,5,6,7,8-oktachloro	291.9	402.2	591.0	113.35	0.68	−4.50	10.07

Table 6. Composition of Equilibrium Mixtures (Mole Fractions) of Polychlorinated Biphenylenes

T/K	298	400	600	800	1000
2-chlorobiphenylene	0.528	0.517	0.507	0.503	0.500
3-chlorobiphenylene	0.472	0.483	0.493	0.497	0.500
1,2-dichlorobiphenylene	0.011	0.018	0.029	0.037	0.043
1,3-dichlorobiphenylene	0.006	0.012	0.023	0.031	0.037
1,4-dichlorobiphenylene	0.110	0.117	0.122	0.123	0.123
1,5-dichlorobiphenylene	0.107	0.115	0.121	0.122	0.122
1,6-dichlorobiphenylene	0.005	0.010	0.018	0.024	0.029
1,7-dichlorobiphenylene	0.006	0.011	0.020	0.027	0.032
1,8-dichlorobiphenylene	0.149	0.150	0.148	0.145	0.143
2,3-dichlorobiphenylene	0.325	0.281	0.238	0.216	0.203
2,6-dichlorobiphenylene	0.130	0.134	0.134	0.131	0.129
2,7-dichlorobiphenylene	0.151	0.152	0.147	0.143	0.140
1,2,3-trichlorobiphenylene	0.000	0.000	0.002	0.005	0.010
1,2,4-trichlorobiphenylene	0.001	0.004	0.014	0.023	0.031
1,2,5-trichlorobiphenylene	0.006	0.014	0.030	0.042	0.050
1,2,6-trichlorobiphenylene	0.005	0.013	0.029	0.042	0.050
1,2,7-trichlorobiphenylene	0.004	0.011	0.026	0.038	0.047
1,2,8-trichlorobiphenylene	0.001	0.003	0.012	0.022	0.031
1,3,5-trichlorobiphenylene	0.230	0.208	0.172	0.148	0.132
1,3,6-trichlorobiphenylene	0.206	0.192	0.164	0.143	0.128
1,3,7-trichlorobiphenylene	0.209	0.196	0.169	0.147	0.132
1,3,8-trichlorobiphenylene	0.046	0.063	0.079	0.084	0.084
1,4,5-trichlorobiphenylene	0.054	0.071	0.086	0.089	0.089
1,4,6-trichlorobiphenylene	0.232	0.206	0.170	0.145	0.128
2,3,5-trichlorobiphenylene	0.003	0.009	0.024	0.036	0.044
2,3,6-trichlorobiphenylene	0.003	0.009	0.023	0.035	0.044
1,2,3,4-tetrachlorobiphenylene	0.000	0.000	0.000	0.002	0.004
1,2,3,5-tetrachlorobiphenylene	0.000	0.000	0.003	0.006	0.010
1,2,3,6-tetrachlorobiphenylene	0.000	0.001	0.003	0.008	0.012
1,2,3,7-tetrachlorobiphenylene	0.000	0.000	0.003	0.006	0.009
1,2,3,8-tetrachlorobiphenylene	0.000	0.000	0.001	0.004	0.006
1,2,4,5-tetrachlorobiphenylene	0.001	0.004	0.011	0.017	0.021
1,2,4,6-tetrachlorobiphenylene	0.004	0.010	0.021	0.027	0.030
1,2,4,7-tetrachlorobiphenylene	0.004	0.010	0.021	0.027	0.030
1,2,4,8-tetrachlorobiphenylene	0.001	0.003	0.010	0.015	0.019
1,2,5,6-tetrachlorobiphenylene	0.000	0.002	0.011	0.021	0.029
1,2,5,7-tetrachlorobiphenylene	0.008	0.017	0.029	0.034	0.036
1,2,5,8-tetrachlorobiphenylene	0.002	0.005	0.013	0.019	0.022
1,2,6,7-tetrachlorobiphenylene	0.000	0.001	0.004	0.008	0.012
1,2,6,8-tetrachlorobiphenylene	0.002	0.005	0.014	0.020	0.024
1,2,7,8-tetrachlorobiphenylene	0.000	0.001	0.004	0.010	0.017
1,3,5,7-tetrachlorobiphenylene	0.673	0.526	0.347	0.252	0.198
1,3,5,8-tetrachlorobiphenylene	0.076	0.086	0.082	0.072	0.063
1,3,6,7-tetrachlorobiphenylene	0.005	0.012	0.024	0.030	0.033
1,3,6,8-tetrachlorobiphenylene	0.144	0.169	0.166	0.148	0.131
1,4,5,8-tetrachlorobiphenylene	0.069	0.118	0.169	0.182	0.181
1,4,6,7-tetrachlorobiphenylene	0.012	0.027	0.050	0.062	0.067
2,3,6,7-tetrachlorobiphenylene	0.000	0.002	0.014	0.030	0.045
1,2,3,4,5-pentachlorobiphenylene	0.000	0.000	0.003	0.008	0.014
1,2,3,4,6-pentachlorobiphenylene	0.000	0.001	0.007	0.014	0.022
1,2,3,5,6-pentachlorobiphenylene	0.001	0.004	0.014	0.025	0.034
1,2,3,5,7-pentachlorobiphenylene	0.028	0.050	0.076	0.086	0.089
1,2,3,5,8-pentachlorobiphenylene	0.028	0.050	0.076	0.086	0.089
1,2,3,6,7-pentachlorobiphenylene	0.006	0.016	0.036	0.050	0.059
1,2,3,6,8-pentachlorobiphenylene	0.000	0.002	0.011	0.021	0.030
1,2,3,7,8-pentachlorobiphenylene	0.005	0.014	0.034	0.047	0.056
1,2,4,5,6-pentachlorobiphenylene	0.000	0.001	0.006	0.013	0.021
1,2,4,5,7-pentachlorobiphenylene	0.011	0.025	0.047	0.060	0.067
1,2,4,5,8-pentachlorobiphenylene	0.441	0.369	0.268	0.209	0.173
1,2,4,6,7-pentachlorobiphenylene	0.085	0.111	0.125	0.122	0.115
1,2,4,6,8-pentachlorobiphenylene	0.387	0.337	0.255	0.203	0.169
1,2,4,7,8-pentachlorobiphenylene	0.008	0.020	0.041	0.055	0.062
1,2,3,4,5,6-hexachlorobiphenylene	0.000	0.001	0.007	0.014	0.021
1,2,3,4,5,7-hexachlorobiphenylene	0.009	0.020	0.038	0.049	0.055
1,2,3,4,5,8-hexachlorobiphenylene	0.003	0.012	0.036	0.059	0.076
1,2,3,4,6,7-hexachlorobiphenylene	0.001	0.006	0.024	0.043	0.059
1,2,3,5,6,7-hexachlorobiphenylene	0.003	0.010	0.032	0.054	0.070
1,2,3,5,6,8-hexachlorobiphenylene	0.018	0.034	0.055	0.064	0.067
1,2,3,5,7,8-hexachlorobiphenylene	0.015	0.029	0.051	0.061	0.066
1,2,3,6,7,8-hexachlorobiphenylene	0.000	0.003	0.014	0.030	0.045
1,2,4,5,6,8-hexachlorobiphenylene	0.496	0.456	0.377	0.315	0.272
1,2,4,5,7,8-hexachlorobiphenylene	0.453	0.429	0.366	0.310	0.270
1,2,3,4,5,6,7-heptachlorobiphenylene	0.072	0.132	0.226	0.289	0.331
1,2,3,4,5,6,8-heptachlorobiphenylene	0.928	0.869	0.774	0.711	0.670

The temperature dependence of molar heat capacity in the temperature region from 200 K to 2000 K was described by the following equation

$$C^{\circ}_{pm}/\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K})^3$$

It was found that the main deviation of the temperature dependence of molar heat capacity, described by this equation, does not exceed 1 % for all the compounds studied.

Final thermochemical properties of the polychlorinated biphenylenes, namely, enthalpy of formation and Gibbs energy of formation at 298 K, and constants of the correlating equation of molar heat capacity are listed in the Table 5.

The composition of equilibrium mixtures of polychlorinated biphenylenes with the same number of chlorine atoms in the molecule was calculated from the thermochemical properties. The calculations were done for the temperature region from 298 K to 1000 K. The values of the composition are listed in Table 6. These results can be compared with the relative stabilities of polychlorinated dibenzo-*p*-dioxins, calculated by Wang et al.[19] The agreement increases with the degree of chlorination. Excepting the hexachlorinated molecules, the relative stability of both series of compounds shows a qualitative correspondence, starting from the trichlorinated molecules.

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