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Thermodynamic Properties of Biphenyl Ether in the Ideal Gas State

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Calculations of thermodynamic properties of biphenyl ether in the ideal gas state using the spectral data and molecular parameters, obtained from quantum chemical calculations, were carried out in the temperature region from 250 K up to 2000 K. A new contribution of the group $(C_B)_2{-}O$ was added to the Benson contribution method.

Introduction

Chlorinated and brominated derivatives of biphenyl ether belong to common pollutants. Thermochemical properties of these compounds are not known, and it is not possible to estimate these values by means of the Benson estimation method,[1,2] because this method does not include the contribution of the group $(C_B)_2{-}O$. Biphenyl ether can be the appropriate model compound for estimation of thermochemical values of the pollutants mentioned above.

In the previous paper,[3] thermochemical values of methoxybenzene in the ideal gas state were calculated from molecular parameters. The aim of this work is to calculate thermochemical values of biphenyl ether.

Enthalpy of Formation

Cass and co-workers[4] obtained a combustion enthalpy of solid biphenyl ether at 298.15 K of −6113.24 kJ mol^{-1}; the older values by Furukawa et al.[5] of formation enthalpy at the same temperature are −32.11 kJ mol^{-1} for solid biphenyl ether and −14.99 kJ mol^{-1} for liquid biphenyl ether. The vaporization enthalpy of biphenyl ether, obtained from calorimetric measurements,[6] is 66.9 kJ mol^{-1}. Ambrose et al.[7] reported the value obtained from the vapor pressure measurements[8] as 65 kJ mol^{-1}. From the work of Furukawa et al.,[5] it follows that the value of enthalpy of fusion is 17.22 kJ mol^{-1} while the value 16.16 kJ mol^{-1} is presented in the later work by Donnelly et al.[9]

The value 44.98 kJ mol^{-1} for standard formation enthalpy of gaseous biphenyl ether was obtained in this work by means of a combination of combustion enthalpy,[4] vaporization enthalpy,[6] molar heat of fusion,[9] and standard formation enthalpies of water and carbon dioxide, available in the standard tables.[11] This value differs from the value 52 kJ mol^{-1} presented by Domalski and Hearing[10] and obtained from enthalpy of formation of liquid biphenyl ether.[5] The reasons for this disagreement is the different value of combustion enthalpy of solid biphenyl ether, −6119.2 kJ mol^{-1} (ref 5). Further, Furukawa et al.[5] performed measurements of combustion enthalpy at 30 °C, and their values of formation enthalpies at 298 K were recalculated. The obtained value 44.98 kJ mol^{-1} of standard formation enthalpy of gaseous biphenyl ether was used for further calculations.

Table 1. Wave Numbers of Vibrations in Biphenyl Ether, Used for Calculation of Thermodynamic Values

type	wavenumber/cm^{-1}	ref	type	wavenumber/cm^{-1}	ref
CH	3089	12	CH	1023	12
ν(CH)	3089	12	ring	1005	13
CH	3089	12	ring	1003	12
ν(CH)	3089	12	γ(CH)	977	13
CH	3075	12	γ(CH)	979	12
CH	3075	12	γ(CH)	961	12
CH	3068	12	γ(CH)	961	12
CH	3040	12	γ(CH)	904	12
ν(CH)	3027	12	γ(CH)	895	13
ν(CH)	3015	12	γ(CH)	865	13
CC	1600	12	γ(CH)	820	13
CC	1593	12	χ sens	794	13
ν(CC)	1591	12	χ sens	794	13
ν(CC)	1585	12	γ(CH)	747	13
CC	1487	12	γ(CH)	749	12
CC	1487	12	ϕ(CH)	690	13
ν(CC)	1455	12	ϕ(CH)	660	13
ν(CC)	1455	12	α(CCC)	617	14
ν(CC)	1335	13	α(CCC)	604	14
ν(CC)	1330	13	χ sens	565	14
β(CH)	1294	12	χ sens	499	14
β(CH)	1280	13	χ sens	481	12
χ sens	1243	13	ϕ(CC)	478	14
χ sens	1198	13	χ sens	416	14
CH	1175	13	ϕ(CC)	395	14
CH	1162	13	χ sens	312	14
β(CH)	1153	12	χ sens	247	14
β(CH)	1153	12	χ sens	220	14
β(CH)	1072	12	χ sens	215	12
β(CH)	1070	13	COC	90	14
CH	1022	13			

Molecular Vibrations

Keaton, Feairheller, and Lippincott[12] measured most of the vibrational wavenumbers of biphenyl ether in the solid state. Horák and Josefi[13] reported several molecular vibrations of gaseous biphenyl ether. The work of Keaton, Feairheller, and Lippincott[12] was taken as a basis, and those wavenumbers, which differ in the solid and gaseous states, were taken from the work of Horák and Josefi.[13] Low-frequency vibrations, measured by Baraldi, Gallinela, and Scoponi,[14] completed this collection. These wavenumbers and their assignments are listed in the Table 1. Only 61 wavenumbers are presented, while the whole number of fundamental vibrations of biphenyl ether is 63. The last two vibrations correspond to internal rotation. While the biphenyl ether molecule contains two benzene groups, the molecule executes two internal rotations.

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Table 2. Comparison of the Calculated Values of Molecular Geometry Parameters with the Spectroscopic Values

parameter	exp	ref	calc
r(C−O) (nm)	0.1332	15	0.133
	1.387	16	
r(C−C) (nm)	0.1398	15	0.138
	0.1396	16	
r(C−H) (nm)	0.1122	15	0.1076
	0.1106	16	
∠CCC (deg)	118−120	16	120
∠CCO (deg)	122	16	120.5
∠CCO (deg)	117	16	120.5
∠COC (deg)	117.5	15	123
	120.5	16	
torsion angle (deg)	90	17	78
	96	15	

Table 3. Calculated Molecular Parameters of Biphenyl

	conformer 1	conformer 2
I_A (kg m^2)	3.740×10^{-45}	5.456×10^{-45}
I_B (kg m^2)	3.165×10^{-44}	2.029×10^{-44}
I_C (kg m^2)	3.248×10^{-44}	2.285×10^{-44}
V (kJ mol^{-1})	67.4	46.2
n	2	2
ΔE (kJ mol^{-1})	−11.05	
I_{RED} (kg m^2)	1.697×10^{-46}	
σ	1	

Molecular Geometry

Complete molecular geometry of the biphenyl ether molecule has not been measured. The values of several bond lengths and bond angles COC, obtained by means of electronography,[15,16] are available. The torsion angle between both phenyl groups was measured using electronography[15] and electronic spectra.[17] The experimental values of the barrier to internal rotation are also absent. The only available values of rotational barrier are those calculated by means of semiempirical quantum chemical methods or by means of ab initio calculations but using less accurate basis (STO-3G, 3-21G) only.[18,19,20]

For these purposes, a new calculation of optimal geometry conformation and barrier to internal rotation in the biphenyl ether molecule were performed by means of the ab initio method. The computer program Gaussian 94[21] and basis 6-31G** (ref 22) were used. Optimization of molecular geometry yields the conformation of the biphenyl ether molecule. The comparison of calculated measured geometric parameters are listed in the Table 2.

Two stable conformers of the biphenyl molecule were found. The former is more stable and corresponds to the conformation, when the first benzene ring and the C−O−C bond lie in the same plane and the torsion angle of the second benzene ring is 78°. The latter is less stable and corresponds to a perpendicular position of the first benzene ring, and the C−O−C bond and the torsion angle of the second benzene ring is 16°. The energy difference between these conformers was found as 11 kJ mol^{-1}.

The rotational barriers were calculated as the energy difference between optimal conformations and conformation with the torsion angle, corresponding to the maximum of energy. Calculation of rotational barriers was performed also with the optimization of geometry except the torsion angle, which was kept constant. The height of the rotational barriers were found as 67.4 kJ mol^{-1} and 46.2 kJ mol^{-1}, respectively.

Obtained geometrical and conformation parameters are summarized in the Table 3.

Calculations of Thermochemical Values

Thermodynamic properties of biphenyl ether were calculated from the vawe numbers, presented in the Table 1, and the molecular parameters, presented in the Table 3, using the rigid rotator model and harmonic oscillator. Because both conformers of the biphenyl ether molecule differ in molecular geometry, the rotational contribution was computed for equilibrium mixture of conformers. The contribution of internal rotation was calculated by means of the tables by Pitzer and Gwinn[23] using the above rotational barriers. Values of entropies of the elements at 298.15 K were taken from the JANAF tables.[11] The calculated values of thermodynamic properties are reported in the Table 4.

Table 4. Thermodynamic Properties of Biphenyl Ether in the Ideal Gas State

T/K	$C°_{pm}$/J·K^{-1}·mol^{-1}	$S°$	$(G° - H°_{298})/T$	$H° - H°_{298}$/kJ·mol^{-1}	$\Delta H°_f$	$\Delta G°_f$
250.00	148.45	381.38	−412.08	−7.67	49.09	141.19
273.15	162.97	395.20	−410.45	−4.17	47.34	158.45
298.15	178.70	410.62	−410.62	0.00	44.98	168.49
300.00	179.86	411.91	−410.58	0.40	44.90	169.27
400.00	242.61	470.97	−417.14	21.53	39.74	214.38
500.00	292.55	530.40	−433.46	48.47	32.62	256.91
600.00	332.65	586.56	−452.75	80.29	29.28	303.15
700.00	364.46	640.26	−475.73	115.17	26.57	349.19
800.00	390.50	690.10	−499.06	152.83	24.75	395.55
900.00	412.14	738.49	−524.07	192.97	23.89	436.48
1000.00	429.97	782.87	−547.79	235.08	23.77	487.25
1100.00	445.23	823.85	−570.19	279.03	24.44	534.57
1200.00	458.16	862.97	−592.77	324.24	25.48	581.15
1300.00	469.20	900.54	−615.56	370.48	26.73	626.67
1400.00	478.78	935.34	−636.86	417.87	28.41	673.21
1500.00	487.00	968.77	−657.96	466.22	30.42	719.08
1600.00	494.07	1000.00	−677.97	515.25	32.50	765.57
1700.00	500.32	1030.09	−697.72	565.03	34.78	811.47
1800.00	505.80	1058.89	−717.03	615.34	36.98	856.93
1900.00	510.63	1086.53	−735.78	666.43	39.67	904.34
2000.00	514.75	1112.59	−753.46	718.26	42.60	968.85

Table 5. Values of Contribution $O-(C_B)_2$ in the Benson Contribution Method

		$C°_{pm}$/J·K^{-1}·mol^{-1}					
$(\Delta_f H°)_{298}$/kJ·mol^{-1}	$S°_{298}$/J·K^{-1}·mol^{-1}	T = 300 K	T = 400 K	T = 500 K	T = 600 K	T = 800 K	T = 1000 K
−85.42	30.87	11.62	12.45	12.27	13.83	17.26	20.33

The temperature dependence of standard enthalpy of formation shows a minimum at temperature about 1000 K. Such a minimum can be found also for similar molecules, containing two phenyl groups, namely, biphenyl and polychlorinated biphenyls.[24]

Standard entropy of gaseous biphenyl ether at 298.15 K was compared with value 233.91 J K^{-1} mol^{-1}, reported by Furukawa et al.[5] for solid biphenyl ether. This value was converted into the ideal gas state. Heat capacities of solid and liquid biphenyl ether[5] and enthalpy of fusion[9] were used. Vaporization enthalpy at normal boiling point was estimated from the Antoine equation constants, reported for biphenyl ether by Collerson et al.[8] By use of these values and the molar heat capacity in Table 4, one obtains the value 425.91 J K^{-1} mol^{-1} for molar entropy of gaseous biphenyl ether, while the value 410.51 J K^{-1} mol^{-1} is presented in Table 4. It leads to the difference about 3.8%.

The values of contribution $O-(C_B)_{2,}$ which is not included in the Benson contribution method, were evaluated from thermodynamic properties, reported in Table 4. The following contribution was taken into account: 10 × $C_B-(H)$, 2 × $C_B-(O)$, and 1 × $O-(C_B)_2$. For the calculation of formation enthalpy, the revised contributions presented by Cohen[25] were used. The external symmetry number was considered as unity and the internal symmetry number as 4. The values of contribution $O-(C_B)_2$ are reported in the Table 5. The value of contribution to formation enthalpy differ by 6.32 kJ mol^{-1} from the value by Cohen,[25] because the value of formation enthalpy presented by Domalski and Hearing[10] was used in the Cohen's work.

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