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Thermochimica Acta 374 (2001) 7–11

thermochimica acta

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Ideal gas thermodynamic properties of biphenyl

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Received 14 November 2000; received in revised form 22 February 2001; accepted 24 February 2001

Abstract

Ideal gas thermodynamic properties for biphenyl have been calculated by statistical thermodynamics method on the basis of available experimental data and the results of recent high-level quantum mechanical calculations. More precise information about the potential barriers to internal rotation and the lowest vibrational frequencies made it possible to achieve the best agreement with calorimetric results in comparison with statistical calculations published earlier. The thermodynamic functions have been also estimated using molecular structure, vibrational frequencies, and potential barrier heights of biphenyl calculated by B3LYP/cc-pVTZ density functional method.

Keywords: Biphenyl; Entropy; Thermodynamic properties

Thermodynamic properties of biphenyl are of great interest today. Their reliable values are essential in estimating the thermodynamic properties of polychlorinated biphenyls, which are environmentally significant compounds.

Biphenyl has been extensively studied over the last decades both experimentally and theoretically to determine the molecular structure, vibrational spectra and potential function for internal rotation. In spite of these extensive studies, there are some uncertainties about the torsional potential and vibrational spectrum assignment. Thermodynamic functions of biphenyl were calculated by statistical thermodynamics method [1–3], but none of these results are in full agreement with the ideal gas entropy values between 298.15 and 700 K determined by Chirico et al. [4] based on calorimetric measurements (Fig. 1). Discrepancies in statistical calculations arise essentially from the absence of experimental gas-phase values for the low-frequency modes, ν_{31} (B_1) and ν_{47} (B_2), and the uncertainty in potential barriers to internal rotation. For the purposes of thermodynamic functions calculation, a certain knowledge of these parameters is of basic importance because even small discrepancies in their values lead to a relatively large change in the calculated entropies.

Among the calculated entropies, the values of Katon and Lippincott [1] are the closest approach to the calorimetric data (Fig. 1). These authors used the values of $\nu_{31} = 120$ and $\nu_{47} = 140\,\mathrm{cm}^{-1}$ and assumed free rotation of biphenyl ($\Delta E = 0$). Better agreement between experimental and calculated entropies was achieved by Chirico et al. [4] using

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0040-6031/01/$ – see front matter
PII: S0040-6031(01)00492-0

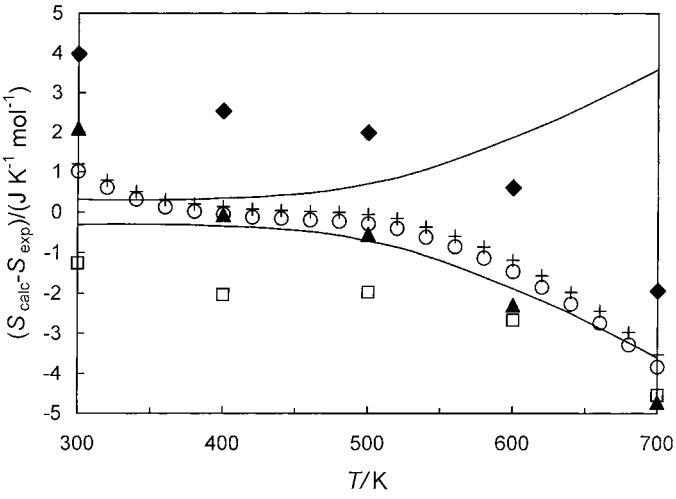

Fig. 1. Deviation of calculated ideal gas entropy values from experimental values [4]. The solid curves represent the uncertainty limits of the calorimetric results. Statistical thermodynamics calculations: (▲) Katon and Lippincott [1]; (□) Aleman and Lielmezs [2]; (◆) TRC tables [3]; (○) this work, molecular parameters from Table 1; (+) this work, B3LYP/cc-pVTZ molecular parameters (see text).

spectroscopic results of Barrett and Steele [5]. Taking the values of $v_{31} = 77\ \text{cm}^{-1}$; $v_{47} = 112\ \text{cm}^{-1}$; $\Delta E_0 = 12.5\ \text{kJ mol}^{-1}$; and $\Delta E_{90} = 0$ (ΔE_0 and ΔE_{90} are the barrier heights towards planar and orthogonal configurations of biphenyl, respectively), a good agreement with calorimetric entropies was obtained except for temperatures below 370 K (see Fig. 8 in [4]; the results were represented in graphical form only). Note that the different wavenumber assignments assumed by Katon and Lippincott [1] and Chirico et al. [4] are approximately counterbalanced by the barrier heights differences, which is why the difference between these two sets of calculated entropies is not so large as one might expect. Because the attempts to achieve the full accord with the calorimetrically derived values have been unsuccessful, Chirico et al. [4] have concluded that further spectroscopic studies were necessary to determine reliable torsional barrier heights and the lowest gas phase fundamentals.

Since the study of Chirico et al. [4], little has been done experimentally to solve the problem of the potential function for internal rotation and the vibrational assignments in the region below $400\ \text{cm}^{-1}$ for gaseous biphenyl, whereas the recent high-level quantum mechanical calculations ([6–10] and references cited therein) yielded the vibrational frequencies and energies of much higher reliability than earlier theoretical results. Based on these calculations, we performed a new ideal gas thermodynamic functions calculation of biphenyl.

From electron diffraction study [11], the potential barrier heights ΔE_0 and ΔE_{90} were estimated to be 6.0 ± 2.1 and $6.5 \pm 2.0\ \text{kJ mol}^{-1}$, respectively. The HF and MP2 ab initio calculations [6–8] predicted that ΔE_0 (13–16 kJ mol^{-1}) was substantially larger than ΔE_{90} (5–7 kJ mol^{-1}). However, the recent MP2 calculation [10] with large basis set, cc-pVQZ, showed that ΔE_0 (9.5 kJ mol^{-1}) was close to ΔE_{90} (8.9 kJ mol^{-1}), which agreed with experimental estimation within the combined errors of the two determinations. The barrier heights obtained from this most precise ab initio calculation were adopted in this work. The structural parameters of biphenyl used in calculations are those from electron diffraction measurements [11]. The vibrational frequencies, except for the lowest ones, were accepted as proposed from the investigation of IR and Raman spectra [5] (Table 1). For two lowest fundamentals, the values of $v_{31} = 92$ and $v_{47} = 118\ \text{cm}^{-1}$ were adopted in this work. These values show the best fit of calculated entropies to the calorimetric data [4] and they are in good agreement with the results of theoretical calculation [9].

Considering that there is a distinct uncertainty in the values of ΔE_0, ΔE_{90}, v_{31}, and v_{47} known from literature, a set of calculations was also carried out by varying these four parameters. It should be noted that

Table 1
Molecular parameters of biphenyl[a]

Vibrational frequencies (cm^{-1})												
A_1	ν_1	3073	B_1	ν_{16}	3070	B_2	ν_{32}	3070	B_3	ν_{48}	3073
	ν_2	3072		ν_{17}	3069		ν_{33}	3069		ν_{49}	3072
	ν_3	3069		ν_{18}	1595		ν_{34}	1567		ν_{50}	3069
	ν_4	1613		ν_{19}	1455		ν_{35}	1430		ν_{51}	1595
	ν_5	1505		ν_{20}	1317		ν_{36}	1337		ν_{52}	1481
	ν_6	1282		ν_{21}	1233		ν_{37}	1266		ν_{53}	1174
	ν_7	1192		ν_{22}	1158		ν_{38}	1155		ν_{54}	1042
	ν_8	1029		ν_{23}	1094		ν_{39}	1072		ν_{55}	1007
	ν_9	1003		ν_{24}	964		ν_{40}	979		ν_{56}	990
	ν_{10}	964		ν_{25}	902		ν_{41}	917		ν_{57}	964
	ν_{11}	838		ν_{26}	735		ν_{42}	778		ν_{58}	838
	ν_{12}	740		ν_{27}	697		ν_{43}	670		ν_{59}	609
	ν_{13}	405		ν_{28}	614		ν_{44}	626		ν_{60}	405
	ν_{14}	307		ν_{29}	486		ν_{45}	543			
	ν_{15}	–[b]		ν_{30}	367		ν_{46}	265			
				ν_{31}	92		ν_{47}	118			

[a] Molecular weight: 154.211; point group: D_2; ground electronic state: $\tilde{X}^1A_1$; symmetry number: 2; product of moments of inertia: $I_AI_BI_C = 805874 \times 10^{-117}$ g^3 cm^6.

[b] Instead of torsional mode $\nu_{15} \approx 70\,cm^{-1}$, the contributions due to the internal rotation about $C_1-C_{1'}$ bond were calculated from the potential: $V(\phi) = (1/2)V_2(1-\cos 2\phi) + (1/2)V_4(1-\cos 4\phi) + (1/2)V_6(1-\cos 6\phi)$, where ϕ is the torsional angle, $V_2 = 47\,cm^{-1}$, $V_4 = -762\,cm^{-1}$ and $V_6 = -99\,cm^{-1}$ ($\Delta E_0 = 9.5$ kJ mol^{-1} and $\Delta E_{90} = 8.9$ kJ mol^{-1}). Reduced moment of inertia: $I_{red} = 7.382 \times 10^{-39}$ g cm^2. Symmetry number for internal rotation: 2.

variations in ΔE_0, ΔE_{90}, ν_{31}, and ν_{47}, allow to reduce the deviations between S°_{calc} and S°_{exp} in either the low-temperature region or the high-temperature region, but not both simultaneously. Moreover, the use of more precise potential function for internal rotation led to entropy values which are in close agreement with entropies calculated by Chirico et al. [4] for potential with $\Delta E_0 = 12.5$ kJ mol^{-1} and $\Delta E_{90} = 0$ (see above). Since it is impossible to improve the agreement between calculated and calorimetric entropies by varying the four parameters, one is inclined to think that other vibrational wavenumbers were assigned incorrectly. This is especially may be true for assignments made from spectra of the crystalline and liquid phases [5]. To check this assumption, the vibrational frequencies of biphenyl, along with the structure and rotational barriers, were calculated in this work at the B3LYP level of density functional theory [12].

Earlier the vibrational spectrum of biphenyl was calculated at HF/STO-3G [13], HF/6-31G*, and B3LYP/6-31G* [9] levels. As was shown by Tsuzuki et al. [10], a large basis set and electron correlation are important in ab initio calculations of this molecule. For this reason, the larger basis set, cc-pVTZ, was used in this work. The following molecular parameters of biphenyl were obtained from B3LYP/cc-pVTZ calculation.

ν_i (cm^{-4}, the values were scaled by a factor of 0.9685) — A_1: 3093, 3081, 3063, 1592, 1495, 1263, 1176, 1023, 991, 961, 836, 734, 409, 305, 63; B_1: 3083, 3067, 1575, 1448, 1320, 1285, 1147, 1074, 977, 903, 737, 698, 610, 488, 360, 92; B_2: 3086, 3070, 1561, 1421, 1322, 1258, 1148, 1070, 977, 921, 778, 694, 622, 544, 260, 124; B_3: 3091, 3077, 3062, 1595, 1475, 1168, 1036, 999, 983, 960, 836, 608, 403

$I_AI_BI_C = 782345 \times 10^{-117}$ g^3 cm^6

$I_{red} = 7.278^{-39}$ g cm^2

$\Delta E_0 = 8.1$ and $\Delta E_{90} = 9.0$ kJ mol^{-1}

As is seen, the calculated barrier heights are close to those obtained at the MP2/cc-pVQZ level [10] and the calculated frequencies support the experimental assignment given in Table 1. In consequence of this, the entropy values calculated with B3LYP/cc-pVTZ molecular parameters agree very closely with the S° values based on experimental vibrational frequencies (Fig. 1).

Thus, the attempts to achieve the full accord with the calorimetrically derived entropy values have been unsuccessful. It is highly improbable that further improvement of molecular parameters of biphenyl will result in better agreement between S°_{calc} and S°_{exp}. At the same time, the calorimetric data may also be subject to refinement. Note that the original calorimetric entropy values for dibenzofuran were recently updated by inclusion of the third virial coefficient [14]. As a result the difference between calculated and experimental entropies was substantially reduced [15].

Compared to published statistical thermodynamics calculations [1–3], the entropy values calculated in this work show the best agreement with calorimetric values (Fig. 1) and can be presently recommended as most reliable. The ideal gas thermodynamic functions of biphenyl (heat capacity C°_p, entropy S°, enthalpy $H^\circ - H^\circ(0)$ and Gibbs energy function $-(G^\circ - H^\circ(0))/T$ were calculated by the standard statistical

Table 2
Ideal gas thermodynamic properties of biphenyl ($p^\circ = 101.325$ kPa)

T (K)	C_p° (J K^{-1} mol^{-1})	S° (J K^{-1} mol^{-1})	$-(G^\circ - H^\circ(0))/T$ (J K^{-1} mol^{-1})	$H^\circ - H^\circ(0)$ (kJ mol^{-1})	$\Delta_f H^\circ$ (kJ mol^{-1})	$\Delta_f G^\circ$ (kJ mol^{-1})	$\log K_f^\circ$
0	0.000	0.000	∞	0.000	210.268	210.268	∞
50	48.096	241.437	202.783	1.933	205.276	212.763	−222.266
100	64.011	279.599	232.296	4.730	199.265	222.797	−116.374
150	84.139	309.180	253.101	8.412	194.754	235.557	−82.026
200	109.211	336.714	270.577	13.227	190.369	249.819	−65.244
298.15	166.417	390.809	301.217	26.712	182.000	280.808	−49.195
300	167.519	391.842	301.773	27.021	181.852	281.422	−48.999
400	224.042	447.949	331.300	46.660	174.678	315.733	−41.229
500	271.389	503.216	360.186	71.515	168.999	351.683	−36.739
600	309.298	556.177	388.476	100.621	164.534	388.646	−33.834
700	339.708	606.222	416.044	133.125	161.080	426.287	−31.809
800	364.497	653.256	442.786	168.376	158.511	464.361	−30.319
900	385.032	697.410	468.651	205.883	156.733	502.705	−29.175
1000	402.250	738.894	493.622	245.272	155.608	541.206	−28.269
1100	416.815	777.935	517.712	286.245	155.058	579.800	−27.532
1200	429.216	814.748	540.946	328.563	154.974	618.416	−26.918
1300	439.833	849.534	563.358	372.029	155.259	657.041	−26.400
1400	448.964	882.471	584.986	416.480	155.810	695.608	−25.953
1500	456.854	913.722	605.869	461.780	156.594	734.154	−25.565

mechanical method [16] using the molecular and spectroscopic constants from Table 1. The calculated values of the enthalpy and entropy were combined with the enthalpy of formation of biphenyl, $\Delta_f H^\circ(g, 298.15\,K) = 182.0 \pm 0.7$ kJ mol^{-1} [4], to derive the values of enthalpy of formation $\Delta_f H^\circ$, Gibbs energy of formation $\Delta_f G^\circ$ and logarithm of the equilibrium constant of formation $\log K_f^\circ$. The last three properties are for formation from C (cr, graphite) and H_2(g) [16]. The chemical thermodynamic properties of biphenyl for temperatures up to 1500 K and a pressure of 101.325 kPa are given in Table 2.

Acknowledgements

We thank Dr. Alexander Belyakov, St. Petersburg Technological Institute, for help in theoretical calculations.

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