CROATICA CHEMICA ACTA 39 (1967) 29

CCA-448

547.789:541.11

Original Scientific Paper

Thermodynamic Functions of Thiadiazoles

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Received October 19, 1966

Using the harmonic oscillator — rigid rotor approximation and the published data on the moments of inertia and the vibrational assignments of 1,3,4-thiadiazole, 1,2,5-thiadiazole, and 1,2,5-thiadiazole-d_2, the thermodynamic functions (enthalpy and free energy functions, entropy and heat capacity) have been calculated. The results are tabulated in Tables III—V. A comparison between the thermodynamic functions calculated in the present work and those of the closely related thiophene is given in Table VI. The vibrational assignment used in the calculation are discussed.

INTRODUCTION

When reliable molecular and spectroscopic data are available, the classical scheme for the calculation of the thermodynamic functions of a molecule (see, for example, Ref. 1 and Ref. 2) is to be prefered over the approximate methods[3–5] or, frequently, the direct experimental measurements which are usually tedious and often even impossible to be carried out.

The harmonic oscillator-rigid rotor approximation (an approximation in which the anharmonicities of the vibrations, the stretching of the molecule as a result of centrifugal forces and the interaction between vibration and rotation are not taken into account) is usually entirely satisfactory in the case of molecules without internal rotation (see Ref. 1, p. 516). Since, in the case of cyclic molecules of the type which are examined here, internal rotation is excluded, the limiting factor in the calculation of thermodynamic functions will be, not the approximation itself, but the accuracy of molecular and spectroscopic data.

The objective of this work was to calculate, using the harmonic oscillator - rigid rotor approximation, some thermodynamic functions (entropy, heat capacity, enthalpy and free energy functions) for two interesting molecules, 1,3,4-thiadiazole and 1,2,5-thiadiazole, and for the deuterated analogue of the latter. The vibrational assignments of these two molecules have appeared recently[6,7] and data on the moments of inertia are also available[8–10]. However, to the best of our knowledge, no thermodynamic data, except for the heat of combustion of 1,3,4-thiadiazole[11], are known.

MOLECULAR AND SPECTROSCOPIC DATA

The three principal moments of inertia of 1,3,4-thiadiazole have been calculated[6] on the basis of the microwave spectrum of Bak *et al.*[8]. The moments of inertia of 1,2,5-thiadiazole have been calculated by Bonham and Momany[9] on the basis of their electron diffraction work, and by Dobyns and Pierce[10] on the basis of the study of their microwave spectra. The moments of inertia of 1,2,5-thiadiazole-d_2 have also been calculated by these latter authors.

The values for the moments of inertia of 1,3,4-thiadiazole, 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 are summarized in Table I.

TABLE I

Moments of inertia of 1,3,4-thiadiazole, 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 *(g. cm.*^{2} *10*$^{-40}$*).*

	1,3,4-thiadiazole[6]	1,2,5-thiadiazole[10]	1,2,5-thiadiazole-d_2[10]
I_a	94.97	98.28	104.35
I_b	151.89	132.50	146.76
I_c	247	230.92	251.24

Complete vibrational assignments have been made by Sbrana and Ginanneschi[6] for 1,3,4-thiadiazole, and by Šoptrajanov and Ewing[7] for 1,3,4-thiadiazole and 1,2,5-thiadiazole-d_2 and are summarized in Table II.

TABLE II

Vibrational assignments of 1,3,4-thiadiazole[6]*, 1,2,5-thiadiazole and 1,2,5-thiadiazole-*d_2*[7].

Species	No.	1,3,4-thiadiazole	1,2,5-thiadiazole	1,2,5-thiadiazole-d_2
A_1	1	3036 (ν_{CH})	3106 (ν_{CH})	2318 (ν_{CD})
	2	1393 (R)	1350 (ν_R)	1294 (ν_R)
	3	1250 (R)	1251 (ν_R)	1183 (ν_R)
	4	1231 (δ_{CH})	1041 (δ_{CH})	849 (δ_{CD})
	5	965 (R)	806 (ν_R)	753 (ν_R)
	6	895 (R)	688 (δ_R)	681 (δ_R)
A_2	7	880 (γ_{CH})	908 (γ_{CH})	735 (γ_{CD})
	8	624 (R)	500 (γ_R)	450 (γ_R)
B_1	9	3075 (ν_{CH})	3108 (ν_{CH})	2320 (ν_{CD})
	10	1500 (R)	1461 (ν_R)	1417 (ν_R)
	11	1198 (δ_{CH})	1227 (δ_{CH})	968 (δ_{CD})
	12	910 (R)	895 (ν_R)	869 (ν_R)
	13	741 (R)	780 (δ_R)	751 (δ_R)
B_2	14	822 (γ_{CH})	838 (γ_{CH})	650 (γ_{CD})
	15	485 (R)	520 (γ_R)	506 (γ_R)

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* ν — stretching; δ — in-plane bending; γ — out-of-plane bending; R — ring (the ring vibrations are not further characterized in Ref. 6 for 1,3,4-thiadiazole)

In spite of the fact that the thiadiazoles under examination belong to the C_{2v} point group and, therefore, have two infrared inactive vibrational modes (those belonging to the A_2 symmetry species), the assignments given in Ref. 6 and Ref. 7 are complete. For 1,3,4-thiadiazole, the two A_2 frequencies were assigned on the basis of the analysis of its liquid, solution and crystal spectra. The frequencies for the two inactive modes of A_2 symmetry for 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 were inferred from the frequencies of several overtone and combination bands and by applying the product rule. Although these modes should be active in the Raman effect, no such bands were found in the Raman spectrum of 1,2,5-thiadiazole[7] which, in this case, only confirmed the assignment made earlier[12] on the basis of infrared data only. As seen from Table II, the frequencies assigned to the A_2 modes of 1,3,4-thiadiazole and 1,2,5-thiadiazole are in rather good agreement, which may be an indication of the correctness of the assignments. Nevertheless, until direct experimental determination of these frequencies in the gaseous phase is made, the frequencies of the A_2 modes represent a weak point in the calculation of the thermodynamic functions.

Another such point, according to this author's opinion, is the assignment of the A_1 fundamentals for 1,3,4-thiadiazole. It seems rather unlikely that a ring deformation mode, corresponding to the ν_6 mode of 1,2,5-thiadiazole, the ν_8 mode of thiophene and furan and the ν_g mode for pyrrole, should lie as high as 895 cm.$^{-1}$, whilst the frequencies for this mode in all above-mentioned compounds lie in the region 608—724 cm.$^{-1}$ [7,13–15]. The bands corresponding to this mode in both 1,2,5-thiadiazole (at 688 cm.$^{-1}$ [7]) and thiophene (at 608 cm.$^{-1}$ [13]) are very weak and difficult to detect. On the other hand, in the gas-phase spectrum of 1,3,4-thiadiazole (see Fig. 1 in Ref. 6) the low-frequency side of the B-type band at 741 cm.$^{-1}$ is broadened as if a weak A-type band (symmetry A_1) were hidden there. The corresponding region in the crystal spectrum (Fig. 3, Ref. 6) is not shown, which is to be regreted since the A_1 band (if there indeed were one) would become clearly visible due to the drastic decrease in width of the 741 cm.$^{-1}$ band. In that case, either the 1250 cm.$^{-1}$ or the 1230 cm.$^{-1}$ band (probably the former) should be assigned to an overtone reinforced by Fermi resonance,

TABLE III

Thermodynamic functions of 1,3,4-thiadiazole (cal. mole^{-1} deg^{-1}).

T (^{0}K)	Contribution	$\frac{H^0 - E^0_0}{T}$	$-\frac{G^0 - E^0_0}{T}$	S^0	C^0_p
298.16	Translation	4.9680	34.3046	39.2726	4.9680
	Rotation	2.9808	20.7192	23.7000	2.9808
	Vibration	1.7207	0.4910	2.2117	6.3209
	Total	9.6695	55.5148	65.1843	14.2697
400	Translation	4.9680	35.7637	40.7317	4.9680
	Rotation	2.9808	21.5951	24.5759	2.9808
	Vibration	3.4423	1.2553	4.6976	10.5463
	Total	11.3911	58.6141	70.0052	18.4951
600	Translation	4.9680	37.7787	42.7467	4.9680
	Rotation	2.9808	22.8037	25.7845	2.9808
	Vibration	6.8586	3.3169	10.1755	16.4957
	Total	14.8074	63.8993	78.7067	24.4445
800	Translation	4.9680	39.2079	44.1759	4.9680
	Rotation	2.9808	23.6612	26.6420	2.9808
	Vibration	9.8225	5.7154	15.5379	20.2757
	Total	17.7713	68.5845	86.3558	28.2245
1000	Translation	4.9680	40.3165	45.2845	4.9680
	Rotation	2.9808	24.3263	27.3071	2.9808
	Vibration	12.1669	8.2498	20.4167	22.6473
	Total	20.1157	72.8926	93.0083	30.5961

and the 965 cm.$^{-1}$ band to a CH bending vibration (having a spectrum of the deuterated compound would clarify this latter point).

Since, obviously, more data than those available from Ref. 6 are needed in order to change the assignment of 1,3,4-thiadiazole, in calculating the thermodynamic functions, the published assignments for all three molecules were taken as correct.

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The method described in detail in Ref. 2 was closely followed in carrying out the calculation of the thermodynamic functions. The results of these calculations are given in Table III, Table IV and Table V for 1,3,4-thiadiazole, 1,2,5-thiadiazole and 1,2,5-thiadiazole-d_2 respectively.

Table VI summarizes the results for the three thiadiazoles and for thiophene, from which the thiadiazoles are derived (by substituting nitrogens for two CH groups) and with which they are isoelectronic. The functions for thiophene are taken from the paper by Rico *et al.*[13]

A very definite trend is observed in the values of all thermodynamic functions in the order: 1,3,4-thiadiazole, 1,2,5-thiadiazole, 1,2,5-thiadiazole-d_2, thiophene. The only exception is for the free energy function at room temperature (298.16 ^{0}K) where the order is: 1,2,5-thiadiazole, 1,3,4-thiadiazole, thiophene, 1,2,5-thiadiazole-d_2. On the other hand, the free energy function is the

TABLE IV

Termodynamic functions of 1,2,5-thiadiazole (cal. mole^{-1} deg^{-1}).

T (^{0}K)	Contribution	$\frac{H^0 - E^o_o}{T}$	$-\frac{G^0 - E^o_o}{T}$	S^0	C^o_p
298.16	Translation	4.9680	34.3046	39.2726	4.9680
	Rotation	2.9808	20.5280	23.5088	2.9808
	Vibration	2.0270	0.6320	2.6590	6.8405
	Total	9.9758	55.4646	65.4304	14.7893
400	Translation	4.9680	35.7637	40.7317	4.9680
	Rotation	2.9808	21.4034	24.3842	2.9808
	Vibration	3.8839	1.4823	5.3662	11.3245
	Total	11.8327	58.6494	70.4821	19.2733
600	Translation	4.9680	37.7787	42.7467	4.9680
	Rotation	2.9808	22.6124	25.5932	2.9808
	Vibration	7.4326	3.7482	11.1808	17.1922
	Total	15.3814	64.1393	79.5207	25.1410
800	Translation	4.9680	39.2079	44.1759	4.9680
	Rotation	2.9808	23.4700	26.4508	2.9808
	Vibration	10.3666	6.3073	16.6739	20.7083
	Total	18.3154	68.9852	87.3006	28.6571
1000	Translation	4.9680	40.3165	45.2845	4.9680
	Rotation	2.9808	24.1351	27.1159	2.9808
	Vibration	12.6722	8.8785	21.5507	22.9377
	Total	20.6210	73.3301	93.9511	30.8865

TABLE V

Thermodynamic functions of 1,2,5-thiadiazole-d_2 *(cal. mole*$^{-1}$ *deg*$^{-1}$*).*

T (°K)	Contribution	$\frac{H^0-E^0_0}{T}$	$-\frac{G^0-E^0_0}{T}$	S^0	C^0_p
298.16	Translation	4.9680	34.3735	39.3415	4.9680
	Rotation	2.9808	20.7956	23.7764	2.9808
	Vibration	2.5902	0.8475	3.4377	8.6302
	Total	10.5390	56.0166	66.5556	16.5790
400	Translation	4.9680	35.8332	40.8012	4.9680
	Rotation	2.9808	21.6714	24.6522	2.9808
	Vibration	4.7086	1.8984	6.6070	13.0296
	Total	12.6574	59.4030	72.0604	20.9784
600	Translation	4.9680	37.8476	42.8156	4.9680
	Rotation	2.9808	22.8800	25.8608	2.9808
	Vibration	8.5341	4.5589	13.0930	18.8013
	Total	16.4829	65.2865	81.7694	26.7501
800	Translation	4.9680	39.2768	44.2448	4.9680
	Rotation	2.9808	23.7375	26.7183	2.9808
	Vibration	11.5601	7.4469	19.0070	22.1925
	Total	19.5089	70.4612	89.9701	30.1413
1000	Translation	4.9680	40.3853	45.3533	4.9680
	Rotation	2.9808	24.4027	27.3835	2.9808
	Vibration	13.9139	10.2905	24.2044	24.3074
	Total	21.8627	75.0785	96.9412	32.2562

one in which the vibrational contribution is the least (at room temperature it represents only about 1.5% of the total value) and which is, therefore, least affected by inaccuracies in the vibrational assignment.

Thus, any far-reaching conclusions do not seem to be justified before the vibrational assignments are reinvestigated and supported by normal coordinate analysis.

TABLE VI

Comparison between the thermodynamic functions of 1,3,4-thiadiazole, 1,2,5-thiadiazole, 1,2,5-thiadiazole-d_2 *and thiophene (cal. mole*$^{-1}$ *deg*$^{-1}$*).*

T (°K)	1,3,4-thiadiazole	1,2,5-thiadiazole	1,2,5-thiadiazole-d_2	Thiophene[12]
1. Enthalpy function, $(H^0-E^0_0)/T$				
298.16	9.67	9.98	10.54	10.65
400	11.39	11.83	12.66	13.10
600	14.81	15.38	16.48	17.78
800	17.77	18.32	19.51	21.64
1000	20.12	20.62	21.86	24.72

TABLE VI (continued)

T (° K)	1,3,4-thiadiazole	1,2,5-thiadiazole	1,2,5-thiadiazole-d_2	Thiophene[12]
2. Free energy function, $-(G^0-E^o_o)/T$				
298.16	55.51	55.46	56.02	55.93
400	58.61	58.65	59.40	59.40
600	63.90	64.14	65.29	65.62
800	68.58	68.98	70.46	71.28
1000	72.89	73.33	75.08	76.45
3. Entropy, S^0				
298.16	65.18	65.43	66.56	66.58
400	70.01	70.48	72.06	72.50
600	78.71	79.52	81.77	83.40
800	86.36	87.30	89.97	92.92
1000	93.01	93.95	96.94	101.18
4. Heat capacity, C^o_p				
298.16	14.27	14.79	16.58	17.40
400	18.50	19.27	20.98	22.98
600	24.44	25.14	26.75	30.65
800	28.22	28.65	30.14	35.39
1000	30.60	30.89	32.26	38.61

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ИЗВОД

Термодинамички функции на тиадиазоли

Б. Шоптрајанов

Врз основа на објавените податоци за моментите на инерција и вибрационите асигнации за 1,3,4-тиадиазол, 1,2,5-тиадиазол и 1,2,5-тиадиазол-d_2 пресметани се некои термодинамички функции (функциите на енталпијата и слободната

енергија, ентропијата и топлинскиот капацитет) за овие молекули. Моделот на хармоничен осцилатор и крут ротор е употребен при пресметнувањето. Резултатите се дадени во Таблиците III—V. Термодинамичките функции пресметани во оваа работа и термодинамичките функции за сродниот тиофен се споредени во Таблица VI. Критички се разгледани вибрационите асигнации употребени при пресметнувањето на термодинамичките функции на тиадиазолите.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ

Примено 19. октомври, 1966.