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Thermodynamic Functions of 1,2,4-Oxadiazole. Comparison with Related Molecules

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The usual thermodynamic functions, namely the enthalpy function (reduced enthalpy), $(H^\circ - E_0^\circ)/T$, free energy function (reduced free energy), $-(G^\circ - E_0^\circ)/T$, entropy, S° and heat capacity, C_p° of 1,2,4-oxadiazole were calculated for one atmosphere pressure and assuming ideal gaseous behaviour throughout the temperature range 298.16—1000° K. The rigid rotator — harmonic oscillator approximation was used in combination with published molecular and spectroscopic data. A slight modification of the published vibrational assignment of the molecule is suggested and the calculations were carried out using both sets of fundamental frequencies. The results are compared with the values obtained previously for the related molecules furan, isoxazole, oxazole, 1,2,5-oxadiazole and 1,3,4-oxadiazole.

INTRODUCTION

We have recently reported the calculation of the thermodynamic functions of some *O*- and *O,N*-containing five-atomic heterocyclic molecules (furan and deuterated furans[1] and oxazole and isoxazole[2]) as well as those of *S*- and *S,N*-containing molecules of the same type[3,4]. As a further step we now report the calculations for a related molecule, 1,2,4-oxadiazole, the thermodynamic functions of two other oxadiazoles (1,2,5- and 1,3,4-oxadiazole) having already been calculated by other authors[5,6].

MOLECULAR AND SPECTROSCOPIC DATA

The moments of inertia of 1,2,4-oxadiazole ($I_a = 81.176.10^{-40}$, $I_b = 83.144.10^{-40}$ and $I_c = 164.430.10^{-40}$ g. cm^2) were evaluated from the rotational constants derived by Griffiths *et al.*[7] from the microwave spectrum and were used to calculate the rotational contribution to the free energy and entropy.

The fundamental frequencies used to evaluate the vibrational contribution to the thermodynamic functions were those reported by Zecchina *et al.*[8] whose assignment seems rather convincing, except, perhaps, for the out-of-plane CH bending modes. In this latter case, however, we feel that the sharp band at 855 cm^{-1} (Q-branch of a C-type band?) would be a better choice for assignment to an out-of-plane CH bending mode than the shoulder at 941 cm^{-1} as proposed by the authors[8]. It would also be somewhat better in line with the assignments proposed for similar molecules[5,6,9–12] to have the assignments of the 1289 and 1225 cm^{-1} bands interchanged (which, of course, would not alter the calculated values for the thermodynamic functions). All these

questions could, no doubt, be settled by the analysis of the spectra of the deuterated species which, unfortunately, are presently unavailable. We have, therefore, calculated the thermodynamic functions using both alternatives and report both sets of data.

For the B-type bands the mean of the reported[8] frequencies of the Q-branches was taken as the value for the corresponding fundamental frequency.

The original assignment (with our alternatives placed in brackets) for the fundamental frequencies of 1,2,4-oxadiazole as used in the calculations is summarized in Table I.

TABLE I

Vibrational Assignment of 1,2,4-Oxadiazole[8,*]

Species	No.	Frequency (cm^{-1})	Approximate description
A′	1	3147	ν_{CH}
	2	3076	ν_{CH}
	3	1560	ν_R
	4	1430	ν_R
	5	1365	ν_R
	6	1289	ν_R [δ_{CH}]
	7	1225	δ_{CH} [ν_R]
	8	1125	ν_R (breathing)
	9	1093	δ_{CH}
	10	956	δ_R
	11	858	δ_R
A″	12	941 [886]	γ_{CH}
	13	886 [855]	γ_{CH}
	14	649	γ_R
	15	618	γ_R

* For the choice of frequencies see text. The abbreviations mean: ν — stretching vibration; δ — in-plane bending vibration; γ — out-of-plane bending vibration; R — ring mode.

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The thermodynamic functions of 1,2,4-oxadiazole were calculated assuming an ideal gaseous behaviour and one atmosphere pressure. Two sets of values were calculated: one using the assignment proposed by Zecchina *et al.*[8] and the other using 855 cm^{-1} as a fundamental frequency instead of 941 cm^{-1}. Since no experimental thermodynamic data are available with which our calculated values could be compared, both sets of values are listed (rounded to two decimal places) in Table II. This table contains, for purposes of comparison, also the values previously obtained for the related molecules furan[1], oxazole[2], isoxazole[2], 1,2,5-oxadiazole[5] and 1,3,4-oxadiazole[6]. For the two oxadiazoles, the thermodynamic functions above 600° K were calculated in the present work (our calculated values below that temperature were identical with those obtained by Christensen and his co-workers[5,6]). All the details concerning the method, the calculations and the values of the fundamental constants used are to be found in the preceding articles of this series.[1,2]

As seen from Table II, the reduced enthalpy and the heat capacity (*i. e.* the functions dependent on the vibrational contribution only) of furan are

TABLE II

Comparison of the Thermodynamic Functions (cal. deg^{-1} mole^{-1}) *of Furan, Oxazoles, and Oxadiazoles*

T(°K)	Furan[1]	Isoxazole[2]	Oxazole[2]	1,2,4-Oxadiazole*		1,2,5-Oxadiazole[5]	1,3,4-Oxadiazole[6]
1. Enthalpy function, $(H^\circ - E_0^\circ)/T$							
298.16	9.90	9.56	9.55	9,23	9.19	9.41	9.16
300	9.93	9.59	9.58	9.25	9.21	9.44	9.19
400	12.08	11.43	11.41	10.74	10.68	11.10	10.63
500	14.39	13.42	13.39	12.40	12.33	12.87	12.25
600	16.59	15.36	15.33	14.02	13.95	14.56	13.85
700	18.62	17.14	17.10	15.54	15.46	16.11	15.35
800	20.47	18.76	18.72	16.92	16.85	17.50	16.72
900	22.12	20.22	20.18	18.17	18.10	18.75	17.96
1000	23.63	21.54	21.49	19.30	19.23	19.86	19.08
2. Free energy function, $-(G^\circ - E_0^\circ)/T$							
298.16	53.95	55.17	55.11	54.96	54.95	53.68	53.56
300	54.01	55.23	55.18	55.02	55.01	53.74	53.61
400	57.16	58.24	58.17	57.88	57.85	56.67	56.45
500	60.10	60.97	60.93	60.45	60.41	59.34	58.99
600	62.92	63.62	63.55	62.86	62.81	61.84	61.37
700	65.64	66.12	66.05	65.14	65.07	64.20	63.62
800	68.25	68.52	68.44	67.31	67.23	66.45	65.76
900	70.75	70.81	70.73	69.37	69.29	68.58	67.80
1000	73.16	73.01	72.92	71.34	71.25	70.61	69.75
3. Entropy, S°							
298.16	63.85	64.73	64.66	64.19	64.14	63.09	62.72
300	63.95	64.82	64.76	64.27	64.22	63.18	62.80
400	69.24	69.66	69.59	68.62	68.54	67.77	67.08
500	74.49	74.39	74.33	72.85	72.74	72.21	71.24
600	79.52	78.97	78.88	76.88	76.75	76.40	75.22
700	84.26	83.26	83.15	80.68	80.53	80.31	78.96
800	88.71	87.28	87.16	84.23	84.07	83.95	82.47
900	92.88	91.04	90.91	87.54	87.38	87.33	85.76
1000	96.79	94.55	94.42	90.64	90.48	90.47	88.83
4. Heat capacity, C_p°							
298.16	15.63	14.39	14.37	13.11	12.99	13.81	12.91
300	15.74	14.49	14.46	13.18	13.06	13.89	12.98
400	21.22	19.29	19.26	17.22	17.09	18.14	16.94
500	25.77	23.36	23.30	20.70	20.59	21.62	20.39
600	29.34	26.55	26.48	23.49	23.40	24.32	23.18
700	32.17	29.06	28.99	25.69	25.61	26.40	25.39
800	34.45	31.07	31.00	27.44	27.38	28.05	27.16
900	36.33	32.70	32.64	28.85	28.80	29.35	28.59
1000	37.91	34.06	34.00	30.00	29.96	30.43	29.77

* Using the modified (see text) and original[8] assignment respectively.

higher than those of the two oxazoles and these, in turn, are higher than the corresponding functions of the oxadiazoles (the values for 1,2,4-oxadiazole falling between those of the symmetrical oxadiazoles). This is an expected consequence of the decrease of the number of fundamental frequencies in the order: furan, oxazoles, oxadiazoles. This trend is less strictly followed (especially at lower temperatures) for the entropy values and not at all for the reduced free energy (*i. e.* the function least dependent on the vibrational contribution to it). This situation is quite similar to that encountered[4] with thiophene, thiazoles and thiadiazoles, only the absolute values for all therdynamic functions of furan and its derivatives are invariably lower than those of the corresponding sulfur-containing molecules.

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ИЗВОД

Термодинамички функции на 1,2,4-оксадиазол. Споредба со сродни молекули

Б. Шоптрајанов

Обичните термодинамички функции: редуцираната енталпија, редуцираната слободна енергија, ентропијата и топлинскиот капацитет на 1,2,4-оксадиазолот се пресметани за притисок од една атмосфера и идеална гасна состојба во температурното подрачје 298,16—1000° K. Беше употребен моделот за крут ротатор и хармоничен осцилатор, како и објавените молекулски и спектроскопски податоци. Сугерирани се и извесни промени во вибрационата асигнација на молекулата. Резултатите се споредени со вредностите добиени порано за сродните молекули фуран, изоксазол, оксазол, 1,2,5-оксадиазол и 1,3,4-оксадиазол.

ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
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