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Original Scientific Paper

Thermodynamic Functions of Oxazole and Isoxazole

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Some thermodynamic functions (enthalpy, free energy, entropy and heat capacity) of oxazole and isoxazole were calculated (298.16°—1000° K) for the pressure of one atmosphere and ideal gaseous state. The calculated thermodynamic functions are compared with the results obtained previously for the related thiazole and *iso*-thiazole. The values for the two oxygen-containing molecules were found to be appreciably lower than those of the corresponding sulfur-containing heterocycles.

INTRODUCTION

Continuing our work on the calculation of thermodynamic functions of five-atomic heterocyclic compounds^{1,2}, we now report the thermodynamic functions of oxazole and isoxazole. These two molecules are closely related to thiazole and *iso*-thiazole to which one of our previous papers² has been devoted.

As before, the harmonic oscillator, rigid rotator approximation^{3,4} has been used and, in the absence of internal rotation which is excluded for cyclic molecules such as the ones presently considered, the limiting factor determining the accuracy of the calculated thermodynamic functions will be the accuracy of the employed molecular and spectroscopic data.

MOLECULAR AND SPECTROSCOPIC DATA

Moments of Inertia

The principal moments of inertia of oxazole and isoxazole were calculated using the rotational constants derived by Mackrodt *et al.*⁵ from the microwave spectra of these molecules. The values thus obtained are listed in Table I.

TABLE I

Rotational Constants (Mc/sec.)⁵ and Moments of Inertia* (g. cm² · 10⁻¹⁰) of Oxazole and Isoxazole

	A	B	C	I _a	I _b	I _c
Oxazole	10050.94	9645.70	4919.40	83.49	87.00	170.58
Isoxazole	9786.24	9575.07	4836.95	85.75	87.64	173.49

* I = 8.39142 · 10⁻³⁵/B (cf. Ref. 6, p. 670)

As seen from Table I, both oxazole and isoxazole have the two smallest moments of inertia nearly equal, *i. e.* they are only slightly asymmetric oblate top molecules. The microwave work of Mackrodt *et al.*⁵ indicated also that the two molecules are planar (molecular symmetry C_s).

Vibrational Assignments

Two vibrational assignments for oxazole have appeared recently: one by Borello *et al.*⁷, based on the analysis of the vapor and liquid infrared spectra, and the other by Sbrana and his co-workers⁸, based on the study of the vapor, liquid, crystal and solution infrared spectra as well as the Raman spectrum of the liquid phase. These two assignments agree more or less, except for the ν_{10} and ν_{13} modes which are placed by Borello *et al.*⁷ at 1480 and 706 cm^{-1} and by Sbrana *et al.*⁸ at 1082 and 858 cm^{-1} respectively. As pointed out⁸, the 1480 cm^{-1} band could easily be explained as a combination, and placing the ν_{13} mode around 860 cm^{-1} is much better in line with the assignment of this mode in the spectra of the related molecules furan⁹, 1,2,4-oxadiazole¹⁰ and 1,2,5-oxadiazole^{11,12}. The assignment by Sbrana *et al.*⁸ was, therefore, adopted and used in the calculations. This assignment is listed in Table II.

TABLE II
Vibrational Assignments for Oxazole⁸ and Isoxazole¹⁶

Species	No.	Oxazole	Isoxazole	Approximate description
A'	1	3168	3140	CH stretching
	2	3148	3128	CH stretching
	3	3099	3086	CH stretching
	4	1545	1560	Ring
	5	1509	1432	Ring
	6	1331	1373	Ring
	7	1260	1217	CH bending
	8	1145	1128	CH bending
	9	1096	1100	CH bending
	10	1082	1089	Ring breathing
	11	1053	1021	Ring
	12	910	930	Ring
	13	858	856	Ring
A''	14	900	889	CH deformation
	15	832	872	CH deformation
	16	749	764	CH deformation
	17	644	632	Ring
	18	609	595	Ring

No recent assignment for isoxazole is available in the literature. Some time ago, Califano and his co-workers analyzed the infrared and Raman spectra of isoxazole¹³ and of isoxazole- d_3 ¹⁴, but some uncertainties still remained. Borello *et al.*⁷ recently listed the frequencies of isoxazole they believed to be likely or sure, but left two modes unassigned and, besides, the attribution of the 1033 cm^{-1} Raman value to an out-of-plane CH deformation mode is highly unlikely, as already pointed out by Katritzky and Boulton¹⁵. Fortunately, Dr. Sbrana¹⁶ was kind to communicate to us his unpublished revised set of fundamentals of isoxazole which now agrees definitely better with the assignments for the related molecules⁹⁻¹². This assignment is also listed in Table II.

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The method employed was the same as described in detail by Colthup *et al.*⁴ and used in the preceding papers of this series^{1,2}.

Detailed tables of the harmonic oscillator functions: $x/(e^x - 1)$; $-\ln(1 - e^{-x})$ and $x^2e^x / (e^x - 1)^2$ ($x = hc\nu/kT$, accuracy of x in the tables and in the calculations = 0.001) were calculated by us on an IBM 1130 electronic computer and were used to evaluate the vibrational contributions to the

TABLE III
Thermodynamic Functions of Oxazole (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_p^0
298.16	Translation	4.9680	33.6419	38.6099	4.9680
	Rotation	2.9808	21.0471	24.0279	2.9808
	Vibration	1.6008	0.4234	2.0242	6.4230
	Total	9.5496	55.1124	64.6620	14.3718
300	Translation	4.9680	33.6774	38.6454	4.9680
	Rotation	2.9808	21.0655	24.0463	2.9808
	Vibration	1.6306	0.4333	2.0639	6.5138
	Total	9.5794	55.1762	64.7556	14.4626
400	Translation	4.9680	35.1066	40.0746	4.9680
	Rotation	2.9808	21.9230	24.9038	2.9808
	Vibration	3.4621	1.1453	4.6074	11.3129
	Total	11.4109	58.1749	69.5858	19.2617
500	Translation	4.9680	36.2152	41.1832	4.9680
	Rotation	2.9808	22.5881	25.5689	2.9808
	Vibration	5.4506	2.1314	7.5820	15.3482
	Total	13.3994	60.9347	74.3341	23.2970
600	Translation	4.9680	37.1210	42.0890	4.9680
	Rotation	2.9808	23.1316	26.1124	2.9808
	Vibration	7.3769	3.2976	10.6745	18.5325
	Total	15.3257	63.5502	78.8759	26.4813
700	Translation	4.9680	37.8868	42.8548	4.9680
	Rotation	2.9808	23.5911	26.5719	2.9808
	Vibration	9.1540	4.5683	13.7223	21.0361
	Total	17.1028	66.0462	83.1490	28.9849
800	Translation	4.9680	38.5502	43.5182	4.9680
	Rotation	2.9808	23.9891	26.9699	2.9808
	Vibration	10.7714	5.9002	16.6716	23.0467
	Total	18.7202	68.4395	87.1597	30.9955
900	Translation	4.9680	39.1353	44.1033	4.9680
	Rotation	2.9808	24.3402	27.3210	2.9808
	Vibration	12.2286	7.2530	19.4816	24.6862
	Total	20.1774	70.7285	90.9059	32.6350
1000	Translation	4.9680	39.6587	44.6267	4.9680
	Rotation	2.9808	24.6542	27.6350	2.9808
	Vibration	13.5452	8.6120	22.1572	26.0468
	Total	21.4940	72.9249	94.4189	33.9956

enthalpy, free energy and heat capacity. The values of the fundamental constants used throughout the calculations were those listed by Herzberg⁶. The atomic weights were those based on ¹²C.

The calculated thermodynamic functions: enthalpy, free energy, entropy and heat capacity at one atmosphere pressure for the ideal gaseous state are listed in Table III and Table IV for oxazole and isoxazole respectively. In Table V the values, rounded to two decimal places, are compared with the

TABLE IV
Thermodynamic Functions of Isoxazole (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 _P ⁰
298.16	Translation	4.9680	33.6419	38.6099	4.9680
	Rotation	2.9808	21.0978	24.0786	2.9808
	Vibration	1.6104	0.4290	2.0395	6.4448
	Total	9.5592	55.1688	64.7280	14.3936
300	Translation	4.9680	33.6774	38.6454	4.9680
	Rotation	2.9808	21.1161	24.0969	2.9808
	Vibration	1.6403	0.4391	2.0794	6.5364
	Total	9.5891	55.2326	64.8217	14.4852
400	Translation	4.9680	35.1066	40.0746	4.9680
	Rotation	2.9808	21.9736	24.9544	2.9808
	Vibration	3.4775	1.1546	4.6321	11.3573
	Total	11.4263	58.2348	69.6611	19.3061
500	Translation	4.9680	36.2152	41.1832	4.9680
	Rotation	2.9808	22.6388	25.6196	2.9808
	Vibration	5.4740	2.1125	7.5865	15.4086
	Total	13.4228	60.9665	74.3893	23.3574
600	Translation	4.9680	37.1210	42.0890	4.9680
	Rotation	2.9808	23.1822	26.1630	2.9808
	Vibration	7.4061	3.3153	10.7214	18.5989
	Total	15.3549	63.6185	78.9734	26.5477
700	Translation	4.9680	37.8868	42.8548	4.9680
	Rotation	2.9808	23.6417	26.6225	2.9808
	Vibration	9.1920	4.5939	13.7859	21.1083
	Total	17.1408	66.1224	83.2632	29.0571
800	Translation	4.9680	38.5502	43.5182	4.9680
	Rotation	2.9808	24.0397	27.0205	2.9808
	Vibration	10.8110	5.9281	16.7391	23.1165
	Total	18.7598	68.5180	87.2778	31.0653
900	Translation	4.9680	39.1353	44.1033	4.9680
	Rotation	2.9808	24.3908	27.3716	2.9808
	Vibration	12.2727	7.2887	19.5615	24.7541
	Total	20.2216	70.8148	91.0364	32.7029
1000	Translation	4.9680	39.6587	44.6267	4.9680
	Rotation	2.9808	24.7049	27.6857	2.9808
	Vibration	13.5900	8.6501	22.2401	26.1111
	Total	21.5388	73.0137	94.5525	34.0599

thermodynamic functions for the related thiazole and *iso*-thiazole calculated previously².

As can be seen from Table V, the calculated thermodynamic functions of oxazole are invariably lower than those of isoxazole. The differences, however, are very slight indeed, which is to be expected in view of the close similarity of the moments of inertia and the fundamental frequencies of the two isomeric molecules. On the other hand, the values for the thermodynamic functions

TABLE V
Comparison of the Thermodynamic Functions of Oxazole and Isoxazole with those of Thiazole and *iso*-Thiazole

T (°K)	Oxazole	Isoxazole	<i>iso</i> -Thiazole	Thiazole ²
1. Enthalpy function, $(H^0 - E_0^0)/T$				
298.16	9.55	9.56	—	—
300	9.58	9.59	10.28	10.33
400	11.41	11.43	12.39	12.44
500	13.39	13.42	—	—
600	15.33	15.36	16.51	16.56
700	17.10	17.14	—	—
800	18.72	18.76	19.92	19.95
900	20.18	20.22	—	—
1000	21.49	21.54	22.63	22.65
2. Free energy function, $-(G^0 - E_0^0)/T$				
298.16	55.11	55.17	—	—
300	55.18	55.23	57.13	57.21
400	58.17	58.24	60.37	60.47
500	60.93	60.97	—	—
600	63.55	63.62	66.19	66.31
700	66.05	66.12	—	—
800	68.44	68.52	71.43	71.55
900	70.73	70.81	—	—
1000	72.92	73.01	76.18	76.30
3. Entropy, S^0				
298.16	64.66	64.73	—	—
300	64.76	64.82	67.40	67.53
400	69.59	69.66	72.76	72.91
500	74.33	74.39	—	—
600	78.88	78.97	82.72	82.87
700	83.15	83.26	—	—
800	87.16	87.28	91.35	91.50
900	90.91	91.04	—	—
1000	94.42	94.55	98.81	98.95
4. Heat capacity, C_p^0				
298.16	14.37	14.39	—	—
300	14.46	14.49	16.23	16.31
400	19.26	19.31	21.09	21.13
500	23.30	23.36	—	—
600	26.48	26.55	27.89	27.90
700	28.99	29.06	—	—
800	31.00	31.07	32.02	32.01
900	32.64	32.70	—	—
1000	34.00	34.06	34.75	34.74

of oxazole and isoxazole are appreciably lower than those of the corresponding sulfur-containing molecules, thiazole and *iso*-thiazole.

It should be noted that the values of $-(G^0 - E_0^0) / T$ and S^0 for *iso*-thiazole listed in Table V are by $0.08 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$ lower than those listed in the corresponding table in Ref. 2. This difference originates from the difference between the moments of inertia estimated by us² and the experimentally determined values which became available¹⁷ after our paper was already published. These latter values were used to correct the rotational contributions to the thermodynamic functions (free energy and entropy) of *iso*-thiazole. The difference is, fortunately, not very large and is comparable to the absolute accuracy of the calculated thermodynamic functions. The observed trends, noted in Ref. 2, are not altered by the correction of the thermodynamic functions of *iso*-thiazole.

Note Added in Proof. After this paper was submitted for publication, a paper by Manley and Williams¹⁸ appeared, with calculations of the thermodynamic functions of some five-atomic heterocyclic molecules we have dealt with in the present and previous papers^{1,2}. The differences between the two calculations in some cases (*iso*-thiazole, isoxazole) are apparently due mainly to the different values of the basic molecular and/or spectroscopic data, whereas the small differences (not exceeding 0.5%) encountered even when identical initial data were used should probably be explained as due to differences in the adopted values for the fundamental physical constants.

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ИЗВОД

Термодинамички функции на оксазол и изоксазол

Б. Шоптрајанов

Пресметани се некои термодинамички функции (енталпија, слободна енергија, ентропија и топлински капацитет) во подрачјето $298,16^{\circ}$ — 1000° К за оксазалот и изоксазолот при притисок од една атмосфера и идеална гасна состојба. Пресметнатите термодинамички функции се споредени со порано добиените вредности за сродните молекули тиазол и изо-тиазол. Вредностите за двете молекули што содржат кислород (оксазол и изоксазол) се забележително пониски од оние за соодветните хетероциклични молекули што содржат сулфур.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ

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