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Original Scientific Paper

Thermodynamic Functions of Thiazole and *iso*-Thiazole

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Some thermodynamic functions (the enthalpy and free energy functions, entropy and heat capacity) of thiazole and *iso*-thiazole have been calculated (300–1000° K), using the harmonic-oscillator, rigid-rotor approximation. The reported assignments for the two molecules were used, as were the published values for the moments of inertia of thiazole. Approximate values for the moments of inertia of *iso*-thiazole have been calculated, assuming bond lengths and angles similar to those of thiophene and 1,2,5-thiadiazole. The calculated thermodynamic functions are compared with the results obtained previously for thiadiazoles and thiophene.

INTRODUCTION

We have recently reported¹ the calculation of some thermodynamic functions (enthalpy and free energy functions, entropy and heat capacity) of thiadiazoles. Using the same harmonic-oscillator, rigid-rotor approximation^{2,3}, we now report the same thermodynamic functions for thiazole (I) and *iso*-thiazole (II), two molecules which are closely related to 1,3,4-thiadiazole (III) and 1,2,5-thiadiazole (IV), to which the previous paper¹ has been devoted.



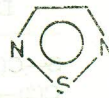
I



II



III



IV

Internal rotation in all these molecules is excluded and so the limiting factor in the calculation of the thermodynamic functions is the accuracy of the molecular and spectroscopic data².

MOLECULAR AND SPECTROSCOPIC DATA

Moments of Inertia

Both thiazole and *iso*-thiazole are asymmetric top molecules, *i. e.* their three principal moments of inertia are different. The values of the moments of inertia for thiazole have been calculated by Bak *et al.*⁴ from the microwave spectrum of this molecule.

The only values for the moments of inertia of *iso*-thiazole we were able to find were those reported by Califano *et al.*⁵, calculated, as stated, assuming

average bond lengths and angles then known in the literature. These values, however, seem to be much too low, much lower, in fact, than those for all other related five-atomic heterocyclic molecules containing sulfur (Table I).

TABLE I
Moments of Inertia of Some Five-Atomic Heterocyclic Molecules Containing Sulfur
($g. cm.^2 \cdot 10^{-40}$).

| | Thiazole ⁴ | iso-Thiazole ⁵ | iso-Thiazole (this work) | Thiophene ⁶ | 1,2,5-Thiadiazole ⁷ | 1,3,4-Thiadiazole ⁸ |
|----------------|-----------------------|---------------------------|--------------------------|------------------------|--------------------------------|--------------------------------|
| I _a | 98.40 | 60.7 | 98.2 | 104.37 | 98.30 | 94.23 |
| I _b | 152.45 | 84.7 | 155.3 | 154.91 | 132.53 | 150.71 |
| I _c | 250.97 | 145.4 | 253.5 | 259.39 | 230.97 | 245.08 |

* The conversion factor from $amu \cdot \text{Å}^2 = 1.6603 \cdot 10^{-40}$

We, nevertheless, attempted to calculate the thermodynamic functions of *iso*-thiazole using the values of Califano *et al.*⁵, but the discrepancies were obvious: whereas the enthalpy function and the heat capacity (which do not depend on the moments of inertia) were very close for thiazole and *iso*-thiazole, the free energy functions differed by 1.5—2 cal. mole⁻¹ deg⁻¹. We, therefore, decided to recalculate the moments of inertia of *iso*-thiazole. The method of Hirschfelder⁹ was used and the structural parameters needed in the calculation were taken from the related thiophene⁶ and 1,2,5-thiadiazole⁷, averaged and slightly rounded. These parameters are listed in Table II. The values of the moments of inertia thus calculated are very close to the ones of other related molecules and were used in the calculation of the thermodynamic functions. The moments of inertia of *iso*-thiazole calculated by us are given in Table I.

TABLE II
Assumed Distances and Angles Used in the Calculation of the Moments of Inertia of *iso*-Thiazole

| Distances (in Å) | | Angles | |
|------------------|------|--------------|--------|
| S—C(2) | 1.71 | SC(2)C(3) | 111.5° |
| C(2)—C(3) | 1.37 | C(2)C(3)C(4) | 112.5° |
| C(3)—C(4) | 1.42 | C(3)C(4)N | 111.5° |
| C(4)—N | 1.33 | SC(2)H(2) | 120° |
| S—N | 1.63 | C(2)C(3)H(3) | 122.5° |
| C—H | 1.08 | NC(4)H(4) | 121° |

Spectroscopic Data

Thiazole and *iso*-thiazole belong to the C_s point group and all of their eighteen normal vibrational modes should be both infrared and Raman active. Nevertheless, one of the ring modes (ν_{13} for thiazole and *iso*-thiazole, ν_6 for 1,2,5-thiadiazole, ν_8 for thiophene) gives rise to a very weak infrared band and is easily observable only in the Raman spectrum.

A reliable vibrational assignment for thiazole has appeared quite recently¹⁰. The assignment, published some time ago, for *iso*-thiazole has, as its major weak point, the placing of the lowest in-plane bending mode (ν_{13}) at 755 $cm.^{-1}$,

instead of in the region between 700 and 600 cm^{-1} where it was subsequently found in all other examined five-atomic heterocyclic molecules containing sulfur¹⁰⁻¹⁴, except in 1,3,4-thiadiazole¹⁵. Fortunately, Dr. Sbrana was kind to communicate to us his revised set of fundamentals for *iso*-thiazole¹¹, which now looks quite convincing and agrees nicely with the assignment of the related 1,2,5-thiadiazole^{12,13}. Of the two bands (at 1071 and 1060 cm^{-1}) which are a typical example of Fermi resonance, the more intense band (that at 1060 cm^{-1}) was taken as a fundamental frequency, although the true value of this fundamental, in the absence of Fermi resonance, would have been somewhat higher. The assignments for thiazole and *iso*-thiazole, used in the present calculation are summarized in Table III.

TABLE III
Vibrational Assignments of Thiazole⁸ and *iso*-Thiazole⁹.

| Species | No. | Thiazole | <i>iso</i> -Thiazole | Description |
|---------|-----|----------|----------------------|-------------------------|
| A' | 1 | 3140 | 3120 | CH stretching |
| | 2 | 3093 | 3099 | CH stretching |
| | 3 | 3065 | 3063 | CH stretching |
| | 4 | 1484 | 1489 | Ring |
| | 5 | 1383 | 1391 | Ring |
| | 6 | 1325 | 1295 | Ring |
| | 7 | 1239 | 1239 | CH in-plane bending |
| | 8 | 1124 | 1060 | CH in-plane bending |
| | 9 | 1043 | 1041 | CH in-plane bending |
| | 10 | 888 | 872 | Ring |
| | 11 | 867 | 819 | Ring breathing |
| | 12 | 759 | 756 | Ring |
| | 13 | 612 | 639 | Ring |
| A'' | 14 | 849 | 910 | CH out-of-plane bending |
| | 15 | 798 | 859 | CH out-of-plane bending |
| | 16 | 717 | 726 | CH out-of-plane bending |
| | 17 | 603 | 590 | Ring |
| | 18 | 467 | 478 | Ring |

CALCULATION OF THE THERMODYNAMIC FUNCTIONS

The method, described in detail by Colthup *et al.*³ and used in the previous paper¹, was used here too. The results are summarized in Table IV and Table V for thiazole and *iso*-thiazole respectively.

As can be seen from Table VI, the calculated thermodynamic functions of thiazole and *iso*-thiazole are very close. This is not unexpected in view of the close correspondence of the moments of inertia and the fundamental frequencies of the two compounds. The thermodynamic functions of *iso*-thiazole have usually smaller values than those of thiazole, but with the heat capacity at higher temperatures the situation is reversed (although there the differences are minimal).

For purposes of comparison Table VI lists also the calculated thermodynamic functions of the related molecules: 1,3,4-thiadiazole, 1,2,5-thiadiazole and thiophene. The results for the former two compounds are taken from

TABLE IV
 Thermodynamic Functions of Thiazole (*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 |
|---------|--------------|-------------------------|-------------------------|----------------|-----------------------------|
| | | T | T | | |
| 300 | Translation | 4.9680 | 34.3008 | 39.2688 | 4.9680 |
| | Rotation | 2.9808 | 22.1695 | 25.1503 | 2.9808 |
| | Vibration | 2.3774 | 0.7360 | 3.1134 | 8.3612 |
| | Total | 10.3262 | 57.2063 | 67.5325 | 16.3100 |
| 400 | Translation | 4.9680 | 35.7300 | 40.6980 | 4.9680 |
| | Rotation | 2.9808 | 23.0270 | 26.0078 | 2.9808 |
| | Vibration | 4.4944 | 1.7107 | 6.2051 | 13.1814 |
| | Total | 12.4432 | 60.4677 | 72.9109 | 21.1302 |
| 600 | Translation | 4.9680 | 37.7443 | 42.7123 | 4.9680 |
| | Rotation | 2.9808 | 24.2356 | 27.2164 | 2.9808 |
| | Vibration | 8.6159 | 4.3276 | 12.9435 | 19.9463 |
| | Total | 16.1647 | 66.3075 | 82.8722 | 27.8951 |
| 800 | Translation | 4.9680 | 39.1735 | 44.1415 | 4.9680 |
| | Rotation | 2.9808 | 25.0932 | 28.0740 | 2.9808 |
| | Vibration | 12.0011 | 7.2865 | 19.2876 | 24.0611 |
| | Total | 19.9499 | 71.5532 | 91.5031 | 32.0099 |
| 1000 | Translation | 4.9680 | 40.2821 | 45.2501 | 4.9680 |
| | Rotation | 2.9808 | 25.7583 | 28.7391 | 2.9808 |
| | Vibration | 14.7006 | 10.2563 | 24.9569 | 26.7899 |
| | Total | 22.6494 | 76.2967 | 98.9461 | 34.7387 |

 TABLE V
 Thermodynamic Functions of iso-Thiazole (*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 |
|---------|--------------|-------------------------|-------------------------|----------------|-----------------------------|
| | | T | T | | |
| 300 | Translation | 4.9680 | 34.3008 | 39.2688 | 4.9680 |
| | Rotation | 2.9808 | 22.1960 | 25.1768 | 2.9808 |
| | Vibration | 2.3270 | 0.7104 | 3.0374 | 8.2783 |
| | Total | 10.2758 | 57.2072 | 67.4830 | 16.2271 |
| 400 | Translation | 4.9680 | 35.7300 | 40.6980 | 4.9680 |
| | Rotation | 2.9808 | 23.0535 | 26.0343 | 2.9808 |
| | Vibration | 4.4417 | 1.6653 | 6.1069 | 13.1405 |
| | Total | 12.3905 | 60.4488 | 72.8392 | 21.0893 |
| 600 | Translation | 4.9680 | 37.7443 | 42.7123 | 4.9680 |
| | Rotation | 2.9808 | 24.2621 | 27.2429 | 2.9808 |
| | Vibration | 8.5752 | 4.2672 | 12.8424 | 19.9441 |
| | Total | 16.5240 | 66.2736 | 82.7976 | 27.8929 |
| 800 | Translation | 4.9680 | 39.1735 | 44.1415 | 4.9680 |
| | Rotation | 2.9808 | 25.1197 | 28.1005 | 2.9808 |
| | Vibration | 11.9712 | 7.2172 | 19.1884 | 24.0665 |
| | Total | 19.9200 | 71.5104 | 91.4304 | 32.0153 |
| 1000 | Translation | 4.9680 | 40.2821 | 45.2501 | 4.9680 |
| | Rotation | 2.9808 | 25.7583 | 28.7391 | 2.9808 |
| | Vibration | 14.6809 | 10.1904 | 24.8713 | 26.8020 |
| | Total | 22.6297 | 76.2573 | 98.8870 | 34.7508 |

Ref. 1 and those for thiophene are from the paper by Rico *et al.*¹⁴. The thermodynamic functions for all these compounds at 300° K have been calculated in the present work. It can be seen that the enthalpy function and the heat capacity (where the translational and rotational contributions are constant)

TABLE VI

Comparison of the Thermodynamic Functions of Thiazole and iso-Thiazole with those of 1,3,4-Thiadiazole, 1,2,5-Thiadiazole and Thiophene (cal. mole⁻¹ deg⁻¹).

| T (° K) | 1,3,4-thiadiazole ¹ | 1,2,5-thiadiazole ¹ | iso-Thiazole | Thiazole | Thiophene ¹⁴ |
|-----------------------------------------------------|--------------------------------|--------------------------------|--------------|----------|-------------------------|
| 1. Enthalpy function, $(H^\circ - E_0^\circ)/T$ | | | | | |
| 300 | 9.70 | 10.01 | 10.28 | 10.33 | 10.69 |
| 400 | 11.39 | 11.83 | 12.39 | 12.44 | 13.10 |
| 600 | 14.81 | 15.38 | 16.51 | 16.56 | 17.78 |
| 800 | 17.77 | 18.32 | 19.92 | 19.95 | 21.64 |
| 1000 | 20.12 | 20.62 | 22.63 | 22.65 | 24.72 |
| 2. Free energy function, $-(G^\circ - E_0^\circ)/T$ | | | | | |
| 300 | 55.57 | 55.52 | 57.21 | 57.21 | 56.03 |
| 400 | 58.61 | 58.65 | 60.45 | 60.47 | 59.40 |
| 600 | 63.90 | 64.14 | 66.27 | 66.31 | 65.62 |
| 800 | 68.59 | 68.98 | 71.51 | 71.55 | 71.28 |
| 1000 | 72.89 | 73.33 | 76.26 | 76.30 | 76.45 |
| 3. Entropy, S° | | | | | |
| 300 | 65.27 | 65.53 | 67.48 | 67.53 | 66.72 |
| 400 | 70.01 | 70.48 | 72.84 | 72.91 | 72.50 |
| 600 | 78.71 | 79.52 | 82.80 | 82.87 | 83.40 |
| 800 | 86.36 | 87.30 | 91.43 | 91.50 | 92.92 |
| 1000 | 93.01 | 93.95 | 98.89 | 98.95 | 101.18 |
| 4. Heat capacity, C_p° | | | | | |
| 300 | 14.35 | 15.16 | 16.23 | 16.31 | 17.52 |
| 400 | 18.50 | 19.27 | 21.09 | 21.13 | 22.98 |
| 600 | 24.44 | 25.14 | 27.89 | 27.90 | 30.65 |
| 800 | 28.22 | 28.65 | 32.02 | 32.01 | 35.39 |
| 1000 | 30.60 | 30.89 | 34.75 | 34.74 | 38.61 |

change in the order: thiadiazoles < thiazoles < thiophene, *i. e.* in the order of the increase of the number of vibrational degrees of freedom. On the other hand, the free energy function of thiophene is smaller than those of thiazole and iso-thiazole, as is the entropy at lower temperatures (at 1000° K the free energy function of thiophene is larger than that of the thiazoles).

It should, however, be borne in mind that the calculated values of the thermodynamic functions are reported to more significant figures than are warranted by their absolute accuracy, that the anharmonicity of the vibrations may be significant at higher temperatures *etc.*, so that making far — reaching

conclusions concerning the order in which the thermodynamic functions change is hardly advisable. Nevertheless we believe that the order of magnitude of the thermodynamic functions is correct and that they can be used for most practical purposes, at least until experimentally determined values become available.

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ИЗВОД

Термодинамички функции на тиазол и изотиазол

Б. Шоптрајанов

Пресметани се некои термодинамички функции (функциите на енталпија и слободна енергија, ентропијата и топлинскиот капацитет) на тиазол и *изо*-тиазол во подрачјето меѓу 300 и 1000° K, употребувајќи го моделот на хармоничен осцилатор и крут ротор, објавените податоци за вибрационите асигнации на горните две молекули, како и податоците за моментите на инерција на тиазолот. Моментите на инерција на *изо*-тиазолот се пресметани, претпоставувајќи дека растојанијата и аглиите кај оваа молекула се слични на оние кај тиофенот и 1,2,5-тиадизолот. Пресметнатите термодинамички функции се споредени со резултатите добиени порано за тиадизолите и тиофенот.

ХЕМИСКИ ИНСТИТУТ
ПРИРОДНО-МАТЕМАТИЧКИ ФАКУЛТЕТ
СКОПЈЕ

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