# Calculation Of Entropy of Azoles by Density Functional Theory Program DGAUSS Method

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***Abstract- I have calculated the entropy of azoles (1,2,3-Triazole, 1,2,4-Triazole, Imidazole, Tetrazole, Pyrrole, Pyrazole, Pentazole,) at different temperatures starting form 200 k. to 600 k. with DFT program. Entropy is the measure of disorder of molecules. As disorder increases, entropy increases. the increment in the entropy of azoles decreases with increase in temperature.***

***Indexed Terms- Azoles, Cache Software, density functional theory, Entropy,***

## I. INTRODUCTION

Entropy is a measure of the number of specific ways in which a system may be arranged, often taken to be a measure of disorder, or a measure of progressing towards thermodynamic equilibrium. The entropy of an isolated system never decreases, because isolated systems spontaneously evolve towards thermodynamic equilibrium, which is the state of maximum entropy. An azole is a class of five-membered nitrogen heterocyclic ring compounds containing at least one other non-carbon atom of either nitrogen, sulfur, or oxygen.

In recent work Rodgers & Armentrout have developed methods to allow the application of quantitative threshold collision induced dissociation methods to obtain accurate thermodynamic is formation on increasingly large system. Many researchers examine the interactions of the family of five-members heterocyclic containing nitrogen. The azoles, with alkalions. The systems were chosen as models of non-covalent interactions with nucleic acids and possibly of selective cation transport through biological membranes. The azoles are building blocks for many antibiotics, anticancer agents and drugs used in the treatment of AIDS. Tetrazoles are used as promoters for synthesis of a variety of biopolymers. The large nitrogen content also makes the azoles important as high energy density compounds useful in explosives and fuels and as clean sources of nitrogen in thin film deposition. Since there is a lot of application of azoles in different fields therefore, we chose this compound for present study. We have calculated the thermodynamic properties entropy of azoles and if, derivatives. The heat of formation can be obtained experimentally, but when a compound is unstable or difficult to purity, experimental heat of formation becomes increasingly difficult to measure. The experimental heat of formation exists for azoles up to three nitrogen atoms. From heat of formation, it is often quite easy to estimate the corresponding heat of reaction at room temperature. Calculations of entropy could provide an extremely useful criterion of reaction mechanism since they depend critically upon the geometry of transition state and the strength and type of bonding init.

## II. MATERIAL AND METHODS

The thermodynamic properties entropy, are calculated by density functional theory program DGauss. This program is available in Cache Software. Cache provides access to MOPAC methods through a windows or Macintosh environment. This section provides reference information about the kinds of computations possible using MOPAC theory and specific information about the Cache computational application, MOPAC. The Cache MOPAC (Molecular Orbital Package) application determines both an optimum geometry and the electronic properties of molecules by solving the Schrodinger equation using the semi-empirical Hamiltonians AM 1, PM3andPM5, development by M.J.S. Dewar and J.J.P. Stewart respectively. Cache also supports the older parameter sets, MNDO and MINDO/3, and the newer parameter set, MNDO-d. In addition, Cache extends AM 1 to AM 1/d.

DGauss can generate thermodynamic properties using statistical mechanics. DGauss calculates an energy that corresponds to the bottom of an energy well. The energy of the molecule at O.K. also includes the Zero-point energy, which is a sum of all the vibrational energies (One-half of the frequency for each vibrational mode). The vibrational frequencies obtained by DGauss are combined with the molecular geometry and symmetry to calculate vibrational, rotational and translational contributions to the entropy, enthalpy and heat capacity of the molecule.

These calculations assume ideal gas behave down too. k, and do not include contributions due to condensed-phase interactions or phase transitions. The standard partition functions are used to express the heat capacity, enthalpy correction (that is, the heat needed to change the ideal gas temperature from o.k. to the temperature under consideration) and entropy at a given temperature as a sum of translational, rotational and vibrational contributions. Low frequency vibrations, those with frequencies smaller than 350 $cm^{-1}$, are excluded from the vibrational contributions as these typically describe free internal rotations. The enthalpy at a given temperature is expressed as a sum of the energy, the zero-point energy and the enthalpy correction.

$$H(T) = E + E_{zeropoint} + \Delta H(T).$$

The enthalpy, H(T), and entropy, S(T) are combined to provide the free energy at a given temperature as G(T)=H(T)-TS(T)

## III. RESULTS AND DISCUSSION

Entropy is the measure of disorder of molecules. As disorder increases, entropy increases. We have reported the entropy of 1,2,3-triazole, 1,2,4 triazole, imdazole, pentazole, pyrazole, pyorle and tetrazole at different temperature in table-1. It is clear form table that entropy increases as the increase of temperature standard value of entropy is takes at 298 K temperature. At 298 K temperature, the entropies of 1,2,3-triazole is 65.237, 1,2’4-triazole is 65.133, imidazole is 66.033, pentazole is 62.947, pyrazole is 65.954, pyrrole is 64.325 and tetrazole is 64.742. In all azoles, the entropy of pentazole is least while entropy of imidazole is highest. The entropy of azoles is in following order Imidazole > Pyrazole > 1,2,3-triazole > 1,2,3-triazole > tetrazole > Pyrrole > Pentazole. The above order of entropy is also found at higher temperatures.

The translational contribution of entropy depends only on the temperature, molecular weight and a number of fundamental constants. While vibrational contribution of entropy depends critically the accuracy of the lower vibrational frequencies. Since the vibrational contribution of entropy at moderate temperatures are relatively small, any errors in the vibrational contribution of entropy are correspondingly reduced in importance in calculating overall entropy. We can also calculate the entropy of reaction as a function of temperature. The entropy of activation, is a measure of the looseness of the transition state and also a reflection of the complexity of the system. If is largely determined by the molecular parameters used to model the energized molecule and the transition state, but also depends upon the threshold energy. Rodgers and Armen trout have calculated the entropies of activation of azoles at 1000k.butinthe present study we have calculated the entropy of azoles at different temperatures starting form200 k. to 600 k. with DFT program. The difference between entropy of 1,2,3-triazole between temperatures 200 k and 220 k is 1.045 cal/mol/kelvin while between temperatures 580 k and 600 k it is 0.909. Thus, the increment in the entropy of 1,2,3-triazole decreases with increase in temperature. Similar trends are also observed in 1,2,4-triazole, imidazole, pentazole, pyrazole, pyrrole and tetrazole. In a number of cases, it is possible to compare the theoretical values of entropy with those determine calorimetrically. For this comparison to be meaningful, the experimental values should be corrected for gas imperfection often the greatest source of uncertainty in these data. The values of entropy determined calorimetrically, spectroscopically and by DFT are in excellent agreement.

TABLE-1

| Molecule | Temperature | Entropy | Molecule | Temperature | Entropy | Molecule | Temperature | Entropy |
|---|---|---|---|---|---|---|---|---|
| 1,2,3-Triazole | 200 | 60.197 | Pyrazole | 200 | 60.57 | Pentazole | 200 | 58.429 |
| | 220 | 61.242 | | 220 | 61.68 | | 220 | 59.39 |
| | 240 | 62.273 | | 240 | 62.78 | | 240 | 60.324 |
| | 260 | 63.298 | | 260 | 63.875 | | 260 | 61.239 |
| | 280 | 64.319 | | 280 | 64.969 | | 280 | 62.143 |
| | 298 | 65.237 | | 298 | 65.954 | | 298 | 62.947 |
| | 300 | 65.339 | | 300 | 66.064 | | 300 | 63.036 |
| | 320 | 66.358 | | 320 | 67.16 | | 320 | 63.921 |
| | 340 | 67.375 | | 340 | 68.256 | | 340 | 64.799 |
| | 360 | 68.391 | | 360 | 69.351 | | 360 | 65.669 |
| | 380 | 69.402 | | 380 | 70.443 | | 380 | 66.531 |
| | 400 | 70.409 | | 400 | 71.532 | | 400 | 67.384 |
| | 420 | 71.41 | | 420 | 72.616 | | 420 | 68.228 |
| | 440 | 72.404 | | 440 | 73.692 | | 440 | 69.063 |
| | 460 | 73.389 | | 460 | 74.761 | | 460 | 69.887 |
| | 480 | 74.366 | | 480 | 75.821 | | 480 | 70.701 |
| | 500 | 75.332 | | 500 | 76.871 | | 500 | 71.503 |
| | 520 | 76.287 | | 520 | 77.911 | | 520 | 72.294 |
| | 540 | 77.232 | | 540 | 78.939 | | 540 | 73.073 |
| | 560 | 78.164 | | 560 | 79.956 | | 560 | 73.841 |
| | 580 | 79.085 | | 580 | 80.96 | | 580 | 74.597 |
| | 600 | 79.994 | | 600 | 81.953 | | 600 | 75.34 |
| 1,2,4-Triazole | 200 | 60.174 | Pyrrole | 200 | 59.004 | | | |
| | 220 | 61.208 | | 220 | 60.086 | | | |
| | 240 | 62.225 | | 240 | 61.165 | | | |
| | 260 | 63.232 | | 260 | 62.248 | | | |
| | 280 | 64.234 | | 280 | 63.338 | | | |
| | 298 | 65.133 | | 298 | 64.325 | | | |
| | 300 | 65.233 | | 300 | 64.435 | | | |
| | 320 | 66.23 | | 320 | 65.537 | | | |
| | 340 | 67.225 | | 340 | 66.645 | | | |
| | 360 | 68.217 | | 360 | 67.756 | | | |
| | 380 | 69.207 | | 380 | 68.868 | | | |
| | 400 | 70.192 | | 400 | 69.978 | | | |
| | 420 | 71.171 | | 420 | 71.086 | | | |
| | 440 | 72.145 | | 440 | 72.19 | | | |
| | 460 | 73.111 | | 460 | 73.287 | | | |
| | 480 | 74.068 | | 480 | 74.377 | | | |
| | 500 | 75.016 | | 500 | 75.458 | | | |
| | 520 | 75.955 | | 520 | 76.53 | | | |
| | 540 | 76.883 | | 540 | 77.592 | | | |
| | 560 | 77.801 | | 560 | 78.642 | | | |

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|---|---|---|---|---|---|---|---|---|
| | 580 | 78.708 | | 580 | 79.682 | | | |
| | 600 | 79.603 | | 600 | 80.71 | | | |
| Imidazole | 200 | 60.586 | Tetrazole | 200 | 59.986 | | | |
| | 220 | 61.71 | | 220 | 60.985 | | | |
| | 240 | 62.823 | | 240 | 61.963 | | | |
| | 260 | 63.931 | | 260 | 62.928 | | | |
| | 280 | 65.037 | | 280 | 63.885 | | | |
| | 298 | 66.033 | | 298 | 64.742 | | | |
| | 300 | 66.144 | | 300 | 64.837 | | | |
| | 320 | 67.25 | | 320 | 65.784 | | | |
| | 340 | 68.356 | | 340 | 66.727 | | | |
| | 360 | 69.459 | | 360 | 67.665 | | | |
| | 380 | 70.559 | | 380 | 68.597 | | | |
| | 400 | 71.655 | | 400 | 69.523 | | | |
| | 420 | 72.745 | | 420 | 70.441 | | | |
| | 440 | 73.827 | | 440 | 71.351 | | | |
| | 460 | 74.901 | | 460 | 72.252 | | | |
| | 480 | 75.965 | | 480 | 73.143 | | | |
| | 500 | 77.02 | | 500 | 74.023 | | | |
| | 520 | 78.063 | | 520 | 74.893 | | | |
| | 540 | 79.094 | | 540 | 75.751 | | | |
| | 560 | 80.114 | | 560 | 76.598 | | | |
| | 580 | 81.121 | | 580 | 77.433 | | | |
| | 600 | 82.116 | | 600 | 78.257 | | | |

## CONCLUSION

The entropy of 1,2,3-triazole, 1,2,4-triazole, imdazole, pentazole, pyrazole, pyorle and tetrazole at different temperature increases as the increase of temperature Entropy is the measure of disorder of molecules. As disorder increases, entropy increases. The translational contribution of entropy depends only on the temperature, molecular weight and a number of fundamental constants. While vibrational contribution of entropy depends critically the accuracy of the lower vibrational frequencies. The entropy of activation, is a measure of the looseness of the transition state and also a reflection of the complexity of the system.

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