Thermodynamic Study of Azoles with Reference to Heat Capacity

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Abstract- In this paper I discuss heat capacity of azoles (1,2,3 – Triazole 1,2,4 –Triazole, Imidazole, Pentazole, Pyrazole, Pyrrole, Tetrazole). Increment in heat capacity of 1,2,3- triazole decreases slightly with the increase of temperature. The similar trends are also observed in 1,2,4-triazole, imidazole, pentazole, pyrazole, pyrrole and tetrazole

Indexed Terms- Azoles, heat capacity, Cache Software, density functional theory

I. INTRODUCTION

Heat capacity, or thermal capacity, is the measurable physical quantity that specifies the amount of heat energy required to change the temperature of an object or body by a given amount. Heat capacity is an extensive property of matter, meaning it is proportional to the size of the system. When expressing the same phenomenon as an intensive property, the heat capacity is divided by the amount of substance, mass, or volume, so that the quantity is independent of the size or extent of the sample. 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. The parent compounds are aromatic and have two double bonds; there are successively reduced analogs (azolines and azolidines) with fewer. One, and only one, lone pair of electrons from each heteroatom in the ring is part of the aromatic bonding in an azole. Names of azoles maintain the prefix upon reduction. The numbering of ring atoms in azoles starts with the heteroatom that is not part of a double bond, and then proceeds towards the other heteroatom. 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 alkaline. The systems were chosen as models of non-covalent interactions with nucleic acids and possibly of selective cation transport through biological membranes. 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 criterian of reaction mechanism since they depend critically upon the geometry of transition state and the strength and type of bonding in it.

II. MATERIAL AND METHODS

The thermodynamic properties heat capacity calculated by density functional theory program DGauss. This program is available in Cache Software. DGauss can generate thermodynamic properties using statistical mechanics. DGauss calculates an energy that corresponds to the bottom of an energy well. Cache makes it is to generate and analyze any number of low energy geometries Cache computer aided chemistry enables to apply mathematical models from classical and quantum mechanics to calculate experimental results. Cache enables create a chemical sample model and perform calculations to discover molecular properties and energy values using computational applications which apply equations from classical mechanics and quantum mechanics. If we need to analyze a structure of unknown geometry, the best place to start is with an exploration of low-energy conformation of the chemical sample. Reaction usually proceeds from the lowest energy conformation or sometimes from any of several low-energy conformation with low barriers for inter conversion. Density functional theory is a completely different, formally rigorous, way of approaching *any* interacting

problem, by mapping it *exactly* to a much easier-to-solve non-interacting problem. In DFT the ground state energy of an atom or a molecule is written in terms of electron density $\rho(r)$, and the external potential $v(r)$ in the form

$E(\rho) = F(\rho) + \int dr\, \rho(r)\, v(r),$

where $F(\rho) = T(\rho) + V_{ee}(\rho)$, $T(\rho)$ is the electronic kinetic energy functional, and $V_{cc}(\rho)$ is the electron-electron interaction energy functional. The minimization of the total energy, subject to the condition that the total number of electrons is fixed,

$N = \int dr\, \rho(r)$

lead to a Euler-Lagrange Equation of the for

$\mu = (\partial E/\delta\rho(r))_v = v(r) + \partial F/\delta\rho(r),$

where the Lagrange multiplier μ, is the chemical potential. The solution of this equation leads to the ground state density, from which one can determine the ground state energy. Parr et. al define the electro negativity as the negative of chemical potential,

$\chi = -\mu = -(\partial E/\partial N)_v$

In the Born-Oppenheimer approximation, we treat the heavy nuclei as fixed points, and we want only to solve the ground-state quantum mechanical problem for the electrons. In regular quantum mechanics, we much solve the Schrodinger equation:

$$\left\{ \frac{1}{2}\sum_{i=1,2}\nabla_i^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \sum_{i=1,2} v_{ext}(\mathbf{r}_i) \right\} \Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2),$$

Where the index *i* runs over the two electrons, and the external potential,

The probability density tells that the probability of finding an electron in d^3r around **r** is n

(r) d^3r. For a system of two *non-interacting* electrons in some potential, $v_s(r)$, chosen somehow to mimic the true electronic system. Because the electrons are non-interacting, their co-ordinates decouple, and their wave function is a simple product of one-electron wave functions, called *orbitals,* satisfying:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),$$

where $\Phi(r_1 - r_2) = \acute{\emptyset}_0(r_1)\,\acute{\emptyset}_0(r_2)$. This is a much simple set of equations to solve, since it only has 3 co-ordinates. Even with many electrons, say *N,* one would still need to solve only a 3-D equation, and then occupy the first *N/2* levels, as opposed to solving a *3N*-coordinate Schrodinger equation. If we can get our non-interacting system to accurately 'mimic' the true system, then we will have a computationally much more tractable problem to solve

The vibrational frequencies obtained by DGauss are combined with the molecular geometry and symmetry to calculate vibrational, rotational and translational contributions to the heat capacity of the molecule. These calculations assume ideal gas behave down to o.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, 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

$H(T) = E + E_{\text{zero point}} + \Delta H(T).$

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

The capacity to absorb heat and store energy is the heat capacity. When system absorbs heat, it goes into kinetic motion at the atoms and molecules. The rate of change of heat with respect to temperature is the heat capacity. The heat capacity of azoles under the frame work of DFT at different temperatures starting from 200 k to 600 k have been presented in the table-1. The rotational contribution of heat capacity remains constant because it depends only on gas constant R. The rotational contribution of heat capacity does not

depend upon temperature. Similarly, the translational contribution of heat capacity remains constant at all temperatures because it also depends on gas constant R. The only vibrational contribution of heat capacity increases with the increases of temperature. The total heat capacity of azoles is presented in the table-1. The heat capacity of 1,2,3-triazole at 200 k temperature is 0.011 k cal/mole/k, it increases with the increase of temperature and because 0.015 kcal/mole/k at 300 k temperature, there is increase of 0.004 kcal/mole/k after increasing 100 k temperature. While heat capacity of 1,2,3-triazole at temperature 500 k is 0.024 kcal/mole/k and it is 0.027 kcal/mole/k at temperature 600 k, there is increase of 0.003 kcal/mole/k after increasing 100 k temperature. Thus, we conclude that increment in heat capacity of 1,2,3-triazole decreases slightly with the increase of temperature. The similar trends are also observed in 1,2,4-triazole, imidazole, pentazole, pyrazole, pyrrole and tetrazole.

TABLE-1: HEAT CAPACITY

Molecule	Temperature	Heat capacity	Molecule	Temperature	Heat capacity	Molecule	Temperature	Heat capacity
1,2,3-Triazole	200	0.011	Pentazole	200	0.01	Tetrazole	200	0.01
	220	0.011		220	0.01		220	0.011
	240	0.012		240	0.011		240	0.012
	260	0.013		260	0.012		260	0.012
	280	0.014		280	0.013		280	0.013
	298	0.015		298	0.013		298	0.014
	300	0.015		300	0.013		300	0.014
	320	0.016		320	0.014		320	0.015
	340	0.017		340	0.015		340	0.016
	360	0.018		360	0.016		360	0.017
	380	0.019		380	0.016		380	0.018
	400	0.02		400	0.017		400	0.018
	420	0.021		420	0.018		420	0.019
	440	0.022		440	0.018		440	0.02
	460	0.023		460	0.019		460	0.021
	480	0.023		480	0.019		480	0.021
	500	0.024		500	0.02		500	0.022
	520	0.025		520	0.02		520	0.022
	540	0.025		540	0.021		540	0.023
	560	0.026		560	0.021		560	0.024
	580	0.027		580	0.022		580	0.024
	600	0.027		600	0.022		600	0.025
1,2,4-Triazole	200	0.01	Pyrazole	200	0.011			
	220	0.011		220	0.012			
	240	0.012		240	0.013			
	260	0.013		260	0.014			
	280	0.014		280	0.015			
	298	0.015		298	0.016			
	300	0.015		300	0.016			
	320	0.016		320	0.018			

	340	0.017		340	0.019			
	360	0.018		360	0.02			
	380	0.019		380	0.021			
	400	0.02		400	0.022			
	420	0.021		420	0.023			
	440	0.021		440	0.024			
	460	0.022		460	0.024			
	480	0.023		480	0.025			
	500	0.024		500	0.026			
	520	0.024		520	0.027			
	540	0.025		540	0.028			
	560	0.026		560	0.028			
	580	0.026		580	0.029			
	600	0.027		600	0.03			
Imidazole	200	0.011	Pyrrole	200	0.011			
	220	0.012		220	0.012			
	240	0.013		240	0.013			
	260	0.014		260	0.014			
	280	0.015		280	0.015			
	298	0.016		298	0.016			
	300	0.017		300	0.016			
	320	0.018		320	0.018			
	340	0.019		340	0.019			
	360	0.02		360	0.02			
	380	0.021		380	0.021			
	400	0.022		400	0.022			
	420	0.023		420	0.023			
	440	0.024		440	0.024			
	460	0.025		460	0.025			
	480	0.025		480	0.026			
	500	0.026		500	0.027			
	520	0.027		520	0.028			
	540	0.028		540	0.029			
	560	0.028		560	0.029			
	580	0.029		580	0.03			
	600	0.03		600	0.031			

CONCLUSION

We conclude that increment in heat capacity of 1,2,3-triazole decreases slightly with the increase of temperature. The similar trends are also observed in 1,2,4- triazole, imidazole, pentazole, pyrazole, pyrrole and tetrazole. The rotational contribution of heat capacity remains constant because it depends only on gas constant R. The rotational contribution of heat capacity does not depend upon temperature. Similarly, the translational contribution of heat capacity remains constant at all temperature because it also depends on gas constant R.

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