Calculation Of Enthalpy of Azoles by The Method of Density Functional Theory Implemented in The Cache Software

P.K. SINGH
Department of Physics, M.L.K. P.G. College, Balrampur, U.P.

Abstract- ***I discuss in this paper internal energy is a state function therefore enthalpy is also a function of state. The enthalpy of azoles is negative. It indicates that a reaction taking place at constant temperature will be exothermic. we conclude that in all the endothermic taking place at a constant temperature, charge in enthalpy has positive sign. Thus, the increment is enthalpy of 1,2,3-triazole increase with increase in temperature. Similar trends are also found in other molecules.***

Indexed Terms- Azoles, Enthalpy, Cache Software, density functional theory

I. INTRODUCTION

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 alkalions. The systems were chosen as models of non-covalent interactions with nucleic acids and possibly of selective cation transport through biological membranes. Enthalpy is a measure of the total energy of a thermodynamic system. It includes the system's internal energy or thermodynamic potential (a state function), as well as its volume and pressure (the energy required to "make room for it" by displacing its environment, which is an extensive quantity). 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, enthalpy 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 enthalpy 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. 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 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, 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.

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

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

ENTHALPY: In Order to study the heat change for reaction taking place at constaint pressure and temperature, chemist introduced a term enthalpy. The enthalpy of a system is defined as sum of internal energy and product of its pressure and volume. The enthalpy of azoles (1,2,3-triazole, 1,2,4-triazole, imidazole, pentazole, pyrazole, pyrrole and tetrazole) have been presented in table- 1 using density functional theory.

Since internal energy is a state function therefore enthalpy is also a function of state. It is not possible to measure its value accurately. However, a change in enthalpy can be measured accurately. It is clear from the table that the enthalpy of azoles is negative. It indicates that a reaction taking place at constant temperature will be exothermic. Thus is all exothermic reaction, the energy will be evolved and given out to the surroundings.

If the change in enthalpy is positive then this shows that the energy will be absorbed form surroundings. That is reaction will be endothermic. Hence, we conclude that in all the endothermic taking place at a constant temperature, charge in enthalpy has positive sign.

The difference between enthalpy 1,2,3-triazole at temperature 200 k and 220 k is 0.219 kcal/mole while between 580 k and 600 k it is 0.527. Thus, the increment is enthalpy of 1,2,3-triazole increase with increase in temperature. Similar trends are also found in other molecules.

The standard value of enthalpy is taken at 298 k temperature. At this temperature the magnitude entropies of azoles are in following order. Pentazole > Tetrazole > 1,2,3-triazole > 1,2,3-triazole > imidazole > Pyrazole > Pyrrole.

The thermodynamic properties like enthalpy and Gibb's free energy of different compounds can also be calculated the phase diagram based on regular solution model (Amrani et-al) In this model the enthalpy ΔH is expressed as:

$\Delta H = \Omega\, x(1-x)$

Where Ω is the interaction parameter which depends on the material. The average value of Ω in the range $o \leq x \leq 1$ as obtained from the fit is 3.814 k cal/mole.

This approach of calculating thermodynamic properties is also based on DFT. But is this calculation full potential linearized augmented place wave (FP-LAPW) method is applied. The results obtained in the present study are very similar with theoretical results.

TABLE-1

Molecule	Temperature	Enthalpy	Molecule	Temperature	Enthalpy	Molecule	Temperature	Enthalpy
1,2,3-Triazole	200	-151950.594	Pentazole	200	-172091.421	Tetrazole	200	-162026.36

	220	-151950.375		220	-172091.219		220	-162026.15
	240	-151950.138		240	-172091.004		240	-162025.93
	260	-151949.882		260	-172090.775		260	-162025.69
	280	-151949.606		280	-172090.531		280	-162025.43
	298	-151949.341		298	-172090.299		298	-162025.18
	300	-151949.31		300	-172090.272		300	-162025.15
	320	-151948.994		320	-172089.997		320	-162024.86
	340	-151948.658		340	-172089.708		340	-162024.55
	360	-151948.303		360	-172089.404		360	-162024.22
	380	-151947.929		380	-172089.085		380	-162023.88
	400	-151947.536		400	-172088.752		400	-162023.52
	420	-151947.126		420	-172088.406		420	-162023.14
	440	-151946.699		440	-172088.047		440	-162022.75
	460	-151946.255		460	-172087.676		460	-162022.34
	480	-151945.796		480	-172087.293		480	-162021.92
	500	-151945.323		500	-172086.901		500	-162021.49

	520	-151944.836		520	-172086.497		520	-162021.05
	540	-151944.336		540	-172086.084		540	-162020.59
	560	-151943.822		560	-172085.662		560	-162020.13
	580	-151943.298		580	-172085.231		580	-162019.65
	600	-151942.761		600	-172084.793		600	-162019.17
1,2,4-Triazole	200	-151965.619	Pyrazole	200	-141877.352			
	220	-151965.402		220	-141877.119			
	240	-151965.168		240	-141876.866			
	260	-151964.917		260	-141876.592			
	280	-151964.646		280	-141876.297			
	298	-151964.386		298	-141876.012			
	300	-151964.356		300	-141875.979			
	320	-151964.047		320	-141875.64			
	340	-151963.719		340	-141875.278			
	360	-151963.372		360	-141874.895			
	380	-151963.005		380	-141874.491			

	400	-151962.621		400	-141874.066			
	420	-151962.22		420	-141873.621			
	440	-151961.801		440	-141873.158			
	460	-151961.367		460	-141872.678			
	480	-151960.916		480	-141872.179			
	500	-151960.452		500	-141871.665			
	520	-151959.973		520	-141871.135			
	540	-151959.481		540	-141870.59			
	560	-151958.977		560	-141870.031			
	580	-151958.459		580	-141869.458			
	600	-151957.931		600	-141868.872			
Imidazole	200	-141886.882	Pyrrole	200	-131799.583			
	220	-141886.646		220	-131799.356			
	240	-141886.39		240	-131799.108			
	260	-141886.113		260	-131798.837			
	280	-141885.814		280	-131798.542			

	298	-141885.527		298	-131798.258			
	300	-141885.493		300	-131798.224			
	320	-141885.15		320	-131797.882			
	340	-141884.785		340	-131797.517			
	360	-141884.399		360	-131797.128			
	380	-141883.992		380	-131796.717			
	400	-141883.565		400	-131796.284			
	420	-141883.118		420	-131795.83			
	440	-141882.653		440	-131795.355			
	460	-141882.169		460	-131794.861			
	480	-141881.669		480	-131794.349			
	500	-141881.153		500	-131793.819			
	520	-141880.621		520	-131793.273			
	540	-141880.074		540	-131792.71			
	560	-141879.513		560	-131792.132			
	580	-141878.939		580	-131791.539			

	600	-141878.352		600	-31791.933			

CONCLUSION

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ACKNOWLEDGEMENT

The authors are highly thankful to the Principal, M.L.K. (P.G.) college, Balrampur, for providing necessary facilities during this work.

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