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Research Article

THERMOCHEMISTRY AND INTERNAL ROTOR CALCULATIONS OF PYRAZOLE DERIVATIVES

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ABSTRACT

Internal rotor calculations and thermochemistry of 3-methyl-4H-pyrazolehas been studied to obtain exact values of heat of formation, bond energies, entropy and heat capacities. Various computational methods (MOPAC, Gaussians) some of the properties have been studied and corrected for internal rotor calculation. Heat of formation is calculated by using MOPAC and Gaussians program. Internal rotor calculations are also done in order to determine rotation potential barrier and its effect on entropies and heat capacities All calculation has been done to study these properties at a range of temperature (298K-1500K). Thermochemical properties of gas phase like ΔH_f, entropy, Gibbs energy and heat capacities values obtained in this study: for parent molecule (in kcal/mol) are (yccdnndc-CH_3) is 55.37, for yccdnndc-ch2j 91.63, for yccjdnnc- CH_3 111.54 and 85.7 for ycjcdnnc- CH_3.

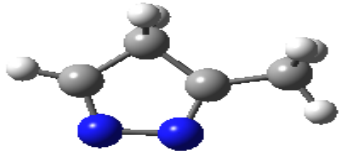
Keywords: Heat of Formation, Enthalpy, 3-methyl-4H-pyrazole, Guassian, MOPAC.

INTRODUCTION

Diazole derivatives particularly pyrazole has wide application including their use in propellant, fuel and component of explosive[1-10]. They have unique advantage of producing N_2 as a product and help to reduce CO_2 especially in carbonic acid erosion in gun barrels[1-4]. Other than that diazole pyrazole also used in the manufacturing of pesticides and synthesis of various synthetic drug molecule. 3-methyl-4H-pyrazole has been chosen for the study due to wide spread use of this kind of molecules and there is no thermochemical study done on this particular molecule [2]. This study focused on, to determine thermochemical properties of 3-methyl-4H-pyrazole and its radicals and incorporate deviation due to internal rotor calucations.

Properties like heat capacities (Cp(T)) and enthalpies (ΔH_f), entropies were first determined for parent molecule ($yC_3H_6N_2$)a than its corresponding radicals, which generated from loss of one hydrogen from the parent structure from the possible site of detachment. Internal rotor analysis also carried out in order to study its potential barrier and its contribution on the heat capacities and entropy. The input matrix for SMCPS got from the frequencies data obtained from Gaussians method using B3LYP/6-31G (d,p)

The Guassian view of parent pyrazole molecule and its radical gives an insight of the structures.



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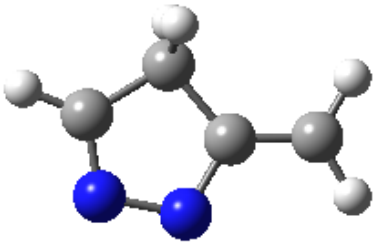
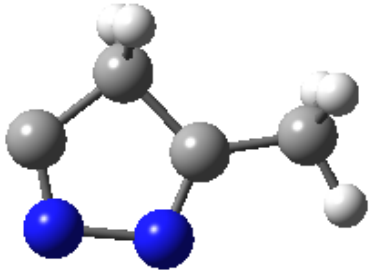
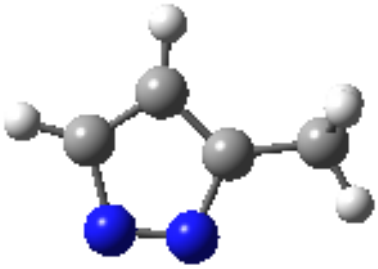


Radical 1



Radical 2



Radical 3

Fig. 1: 3-methyl-4H-pyrazole molecule and corresponding radicals

EXPERIMENTAL

Computational Methods

The choice of method was based on the property need to be determined and the level of accuracy desired. We determined the heat of formation, entropy and heat capacity of 3-methyl-4H-pyrazole and its radicals. The first part of the study was performed to determine the heat of formation by using MOPAC7 PM3 and Gaussians B3LYP/6-31G(d,p). Initial calculations were done using MOPAC by incorporating Z-matrix in the program. Although MOPAC is not so precise method for the calculation but it helped us to make the work reactions and more importantly it provides us template to run the Gaussians program.

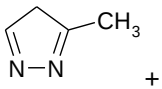
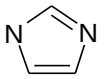
The Z-matrix has been optimized before running MOPAC and Gaussian calculations. Structural parameters for these species are optimized for structure at the B3LYP/6-31G(d,p) level of theory. The MOPAC and Gaussian methods perform initial geometry optimization and frequency calculations with HF theory. By studying the structure of 3-methyl-4H-pyrazole, we designed optimized z-matrix by putting value for the bond length, bond angle, dihedral angle and the connections. The following parameters were obtained using this calculation.

A. Enthalpies of formation: First enthalpies of formation were calculated by using MOPAC and Gaussians calculations. Then work reactions have been designed in such a way that can provide the more accurate heat of formation. Work reactions involved reactant and product with the same bond type. This use of same kind of bond types in all the molecules involved reduced the chances of error to the great extent as reactant and product has same bonding environment. Heat of formation of all reactant and products were determined

$$\Delta H_{rxn} = \sum \Delta H_{products} - \sum \Delta H_{reactants}$$

By using above reaction above equation, experimental ΔH_{rxn} has been determined. Putting the literature value available and ΔH_{rxn}, enthalpy of formation for the parent molecule has been determined. Same methodology were used for the calculating respective heat of formation.

Work reactions were designed one for parent molecule and three for the respective radicals.

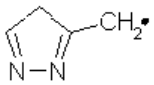
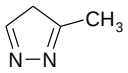
1)  + C_2H_6 →  + C_3H_8

or we can write this equation as in string format

yccdnndc-CH_3 + Ch3Ch3 → ycncdcndc + $CH_3CH_2dCH_3$

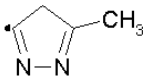
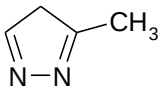
B. Work reaction for radicals:

2) Radical 1:

 +CH_2CHCH_3 →  + CH_2CHCH_2j

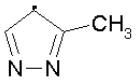
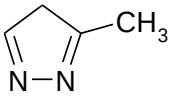
yccdnndc-CH_2j + $CH_3CH_2dCH_3$ → yccdnndc-CH_3 + CH_2dCHCH_2j

3) Radical 2:

 + CH_2CH_2 →  + CH_2CHj

y ccjdnndc-CH_3 +CH_2dCH_2 → yccdnndc-CH_3 + CH2dCHj

4) Radical 3

 + CH_2CHCH_3 →  + CH_2CHCH_2j

y cjcdnndc-CH_3+ CH_2dCHCH_3 ⇒ yccdnndc-ch3 + CH_2dCHCH_2j

C. Entropies and Heat Capacities

Standard entropies, heat capacities and Gibbs energy were determined by incorporating the geometry, symmetry, frequencies, and moments of inertia of the B3LYP/6-31G(d,p) optimized structures in the statistical mechanics SMCPS program. Vibrational frequencies used in SMCPS got from the Gaussian derived frequency values.

RESULT AND DISCUSSION

MOPAC and Gaussian B3LYP calculation were performed to obtain the heat of formation .For MOPAC program, Z-matrix was designed. Parallel calculation were done by applying command thermo and aigout to obtain various physical and thermal properties value and obtained the input program for Guassian. Same Guassian B3LYP carried out for parent molecule including the radicals and all potential reactants employed in work reaction.

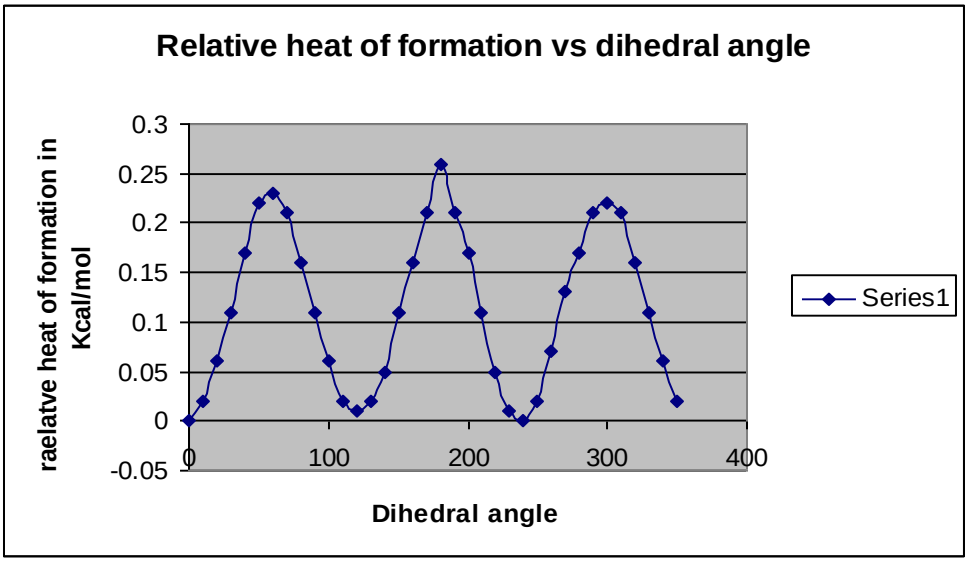


Fig. 2: Relative heat of formation vs dihedral angle

Work reactions were designed to get the ΔHrxn by inputting values obtained from MOPAC and Guassian.separate calculation were made for both ,but using the same work reaction.

Table 1: ΔH_{rxn} reaction obtained after putting value of heat of formation from the MOPAC and Gaussian

Reactions	ΔH_{frxn}(kcal/mol) MOPAC	ΔH_{frxn}(kcal/ mol) B3LYP
yccdnndc-ch3 + ch3ch3⇒ ycncdcndc +ch3ch2dch2	-24.46	-26.16
yccdnndc-ch2j +ch2dchch3 ⇒yccdnndc-ch3 + ch2dchch2j	-5.77	-1.43
y ccjdnndc-ch3 +ch2dch2 ⇒ yccdnndc-ch3 +ch2dchj	-15.25	0.09
y cjcdnndc-ch3+ ch2dchch3⇒ yccdnndc-ch3 + ch2dchch2j	-1.88	0.0

Care was taken to use the reactant with same bonding environment as of the molecule undergoes study

Table 2: Calculated heat of formation calculates by using ΔHrxn value and the resulted heat of formation comes out is presented following.

Species	ΔH_f(kcal mol-1) MOPAC	B3LYP
yccdnndc-ch3	52.77	54.47
yccdnndc-ch2j	94.57	91.13
y ccjdnndc-ch3	126.48	112.84
y cjcdnndc-ch3	90.68	89.7

Moment of inertia

Moments of inertia from Gaussian and MOPAC of parent molecule and its radical has been recorded .As data from Gaussian is much accurate and reliable then MOPAC,hence Gaussian moment of inertia has been used in SMCPS calculation

Table 3: Moment of inertia of pyrazole and its radicals

	Parent Guassian (GHz)	Radical 1 Guassian (GHz)	Radical 2 Gaussian (GHz)	Radical 3 Gaussian (GHz)
A	8.7292107	8.8272233	8.4539830	8.6675295
B	3.4464156	3.7887036	3.3831795	3.7872009
C	2.5483751	2.4612454	2.5174387	2.6790641

For parent molecule (yccdnndc-ch3), Radical 1(yccdnndc-ch2j) Radical 2 (y ccjdnndc-ch3)

SMCPS analysis

Heat capacities and entropy was calculated using SMCPS method. The contribution of internal rotor in the molecule was determined by using VIBIR .By obtaining the data of internal rotor contribution final correction has been done in the heat capacities and entropy.

Table 4: Comparison of heat capacity of MOPAC and SMCPS calcualtion for parent molecule (yccdnndc-ch3)

Temperature	Cp (cal/k/mol)mopac	Cp (cal/k/mol)rotor=1,B3LYP*
298	21.4	19.1
398	27.7	25.6
498	32.9	30.8
598	37.0	35.0
698	40.3	38.3
798	43.0	41.0
898	45.3	43.3
998	47.2	45.2
1098	48.8	46.8
1198	50.2	48.2
1298	51.4	49.4
1398	52.5	50.4
1498	53.4	51.3

We have done SMCPS calculations with rotor and without rotor. The results are presented in table 4 and Figure 1.

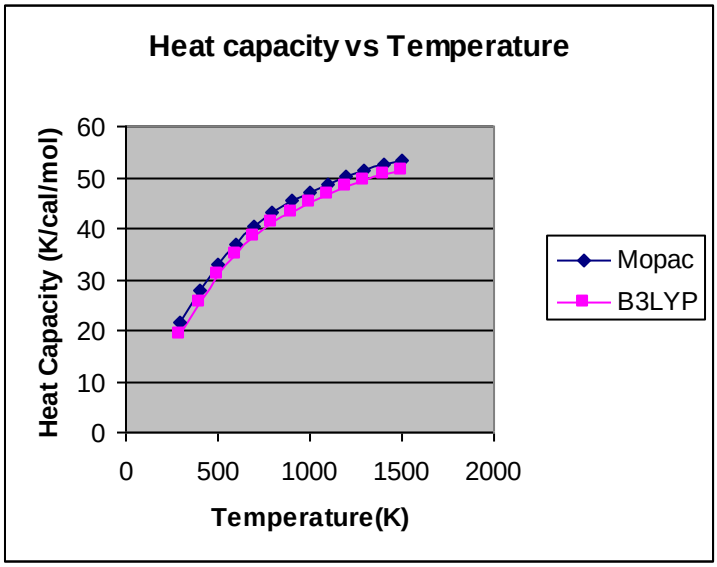


Fig. 2: Heat capacities vs temperature

The difference between heat capacity calculated from both the method was very low, but, the difference is much higher in the entropy calculated from both method as can be seen in Figure 2.

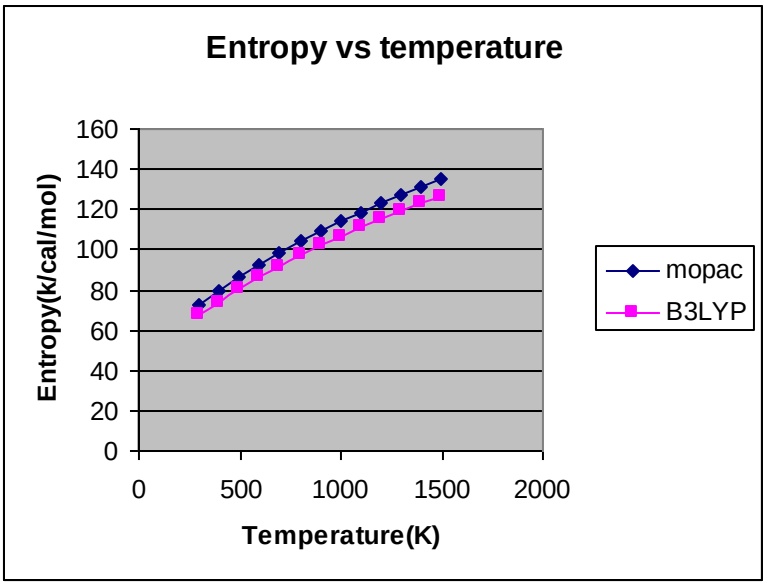


Fig. 3: Comparison of entropy vs temperature

To correct the theomo chemical properties for the variation in internal rotor, we added the internal rotor calculation for the individual molecules and corrected the entropy and enthalpy data (Table 5).

Table 5: Final heat capacities and entropy obtained for the parent molecule and its radicals

Temp(k)	Parent (0 rotor Cp(cal/k/mol)	Parent 1 rotor Cp(cal/k/mol) (1 rotor +vibir)	Parent Entropy (0 rotor)	Parent Entropy (1 rotor +vibir)
300	21.7	20.8	71.7	74.5
400	28.2	27.3	79.0	75.8
500	33.8	32.8	85.9	82.3
600	38.4	37.4	92.5	88.5
700	42.2	41.2	98.7	94.4
800	45.4	44.4	104.6	100.0
900	48.1	47.1	110.1	105.3
1000	50.3	49.2	115.3	110.3
1100	52.3	51.2	120.2	115.0
1200	53.9	52.8	124.8	119.4
1300	55.4	54.3	129.2	123.6
1400	56.6	55.5	133.3	127.6
1500	57.7	56.6	137.3	131.4

CONCLUSION

Isodesmic work reactions were employed to study and reduce the error in the calculations thermochemical properties like heat of formation, Gibbs energy and heat capacity. Specific work reaction has been written by using reactants having the same or somewhat similar bonding environment as of target molecule. This enable us to get the more accurate value of heat of formation of the molecule.

Revised heat capacities, entropy of all molecules including the contribution of rotor

obtained from VIBIR .As we seen above there is difference between heat capacity and entropy obtained for molecules with and without rotor using SMCPS program.

Heat of formation values obtained in this study are the following (in kcal/mol) for parent molecule (yccdnndc-ch3) is 54.47, for yccdnndc-ch2j 91.13, for yccjdnnc-ch3 112.84and 89.7 for ycjcdnnc-ch3.Wheras bond energy for the formation (kcal/mol) of respective radicals are 88.93 (yccdnndc-ch2j),110.47 (yccjdnnc-ch3) and 87.33 (ycjcdnnc-ch3).

This study also shows that there is significant difference in the thermochemical properties value by using Semi empirical method (PM3). So, it is evident that as the molecule goes complex the difference in the mopac and Gaussian goes increase. Hence, the error is high in Mopac analyses when we worked on complex molecule. But, overall for initial calculations Mopac is a useful tool, whereas Gaussian along with smcps and VIBIR are used for the advance level calculations

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