Theoretical thermodynamic study of Pyrazole in the gas phase at the different temperatures

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ABSTRACT

The thermodynamic functions such as enthalpy (H), Gibbs free energy (G) and entropy (S) of Pyrazole was theoretically studied at 5 different temperatures 25, 30, 35, 40 and $45^{\circ}C$ by using Gussian o3, software. First, the structural optimization of isolated Pyrazole was done in the gas phase by appling the Density Functional Theory (B3LYP) level with 3-21G, 6-31G and 6-31+G(d) basis sets. Moreover, vibrational frequencies were calculated in gas phase on the optimized geometries at the same level of theory to obtain enthalpy, Gibbs free energy and entropy at 5 different temperatures.Finally the temperature effects on the thermodynamic functions were discussed.

Keywords: Pyrazole; B3LYP-calculations; Thermodynamic functions

INTRODUCTION

Pyrazole refers both to the class of aromatic ring organic compounds of the heterocyclic series characterized by a 5-membered ring structure composed of three carbon atoms and two nitrogen atoms in adjacent position and to the unsaturated parent compound. The simple member of the Pyrazole family is Pyrazole itself, a compound with molecular formula $C_3H_4N_2$. The Pyrazole compounds are not known to occur in nature; they are usually prepared by the reaction of hydrazines with 1, 3- diketones. Many synthetic Pyrazole compounds are of importance as dyes and medicinals. Among them are: antipyrine, used as a analgesic and febrifuge; tartrazine, most commonly used as a yellow dye for food; muscle relaxing; antidiabetic; antibacterial activities; an anti-inflammatory drug used in treatment of arthritis; and a series of dyes used as sensitizing agents in colour photography[1-6].

Thermodynamics is a branch of natural science concerned with heat and its relation to energy and work. It defines macroscopic variables (such as temperature, internal energy, entropy and pressure) that characterize materials and radiation, and explains how they are related and by what laws they change with time. Thermodynamics describes the average behavior of very large numbers of microscopic constituents, and its laws can be derived from statistical mechanics. Thermodynamics applies to a wide variety

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of topic in science and engineering, phase transitions, chemical reactions, transport phenomena and even black holes. Results of thermodynamic calculations are essential for other fields of physics and for chemistry, chemical engineering, mechanical engineering, cell biology, biomedical engineering and materials science and useful in other fields such as economics [7-8].

In this study, the structural optimization of the heterocyclic compound Pyrazole was investigated. The optimization results of the isolated Pyrazole molecule in the gas phase, at the B3LYP level with 3-21G, 6-31G and 6-31+G (d) basis sets have also been carried out. The calculation about the temperature effects on the stability of Pyrazole was performed appling vibrational frequencies method at B3LYP/6-31+G(d) and then the temperature effects of surrounding were analyzed.

COMPUTATIONAL METHODS
Geometries
All calculations for the optimization and vibrational frequencies of Pyrazole were done with the Gussian 03[13], Ab initio packages at the Density Functional Theory (B3LYP) level of theory. Three basis sets were used including 3-21G, 6-31G and 6-31+G (d). At first, the geometry of Pyrazole was full optimized at the B3LYP/3-21G, 6-31G and 6-31+ G (d) levels of theory in the gas phase. The molecular geometry was obtained by B3LYP/6-31+ G (d) level of optimization for Pyrazole in the gase phase. Then vibrational frequencies were calculated at 5 different temperatures 25, 30, 35, 40 and 45°C.

RESULTS AND DISCUSSION
The geometry optimization of Pyrazole molecule was chosen as the starting step in the gase phase. The Pyrazole was found to be stable in the optimized gas phase at B3LYP/3-21G, 6-31G and 6-31+G (d) level. The results are summarized in Table1.

In accordance with the obtained results, the minimum energy was related to basis set 6-31+G (d) level. Therefore, here the basis set of 6-31+G (d) was selected for the using vibrational frequencies calculations. This calculations were applied for the determining thermodynamics function at 5 different temperatures. The results are peresented in Table2.

Regular alterations were observed concerning thermodynamic functions *versus* temperature. With increasing of the temperature of the Pyrazole in gaseous phase the thermodynamic functions (G) was decreased and (H, S) was increased (Fig1a-c). The Fig.1a shows the plot of the enthalpy H (in kcalmol^{-1}) of Pyrazole versus the temperature. Obviously, the magnitude of H is increase by increasing the temperature. The Fig.1b shows the plot of the Gibbs free energy G (in kcal mol^{-1}) of Pyrazole versus the temperature. The results in Fig.1b show that, with increase of temperature the Gibbs free energy decreases. The Fig.1c shows the plot of the enthropy S (in kcal mol^{-1}) of pyrazole versus the temperature. The entropy values are positive and can be related to the structural stability in gas phase. The results in Fig.1c shows, with increase of temperature the entropy increases.

Thermodynamic analysis
Table 2 displays the calculated relative enthalpy (H), Gibbs free energy (G) and entropy (S) in gas phase for Pyrazole at 5 different temperatures 25, 30, 35, 40 and 45°C. In addition, the plots of calculated relative enthalpy (H), Gibbs free energy (G) and entropy (S) versus the 5 different temperatures are drown in Figs.1a-c respectively. From Table2 and Figs.1 it can be seen that Pyrazole has negative values

of relative enthalpy (H) and Gibbs free energy (G) in gas phase. Also, our results in Table2 and Figs. 1c show that entropy (S) for Pyrazole has positive values. These observations can be related to the structural stability of Pyrazole in gas phase.

Table 1. Absolute calculated results of the conformational energies (E(in kcal mol^{-1})) of Pyrazole obtained by geometry optimization at basis set 6-31+ G (d), 6-31G and 3-21G levels

Basis set	E(kcal mol^{-1})
	Pyrazole
3-21G	-141151.688
6-31G	-141892.713
6-31+G(d)	-141948.219

Table 2. The determining thermodynamic functions of Pyrazole at the 5 different temperatures by using vibrational frequencies calculations

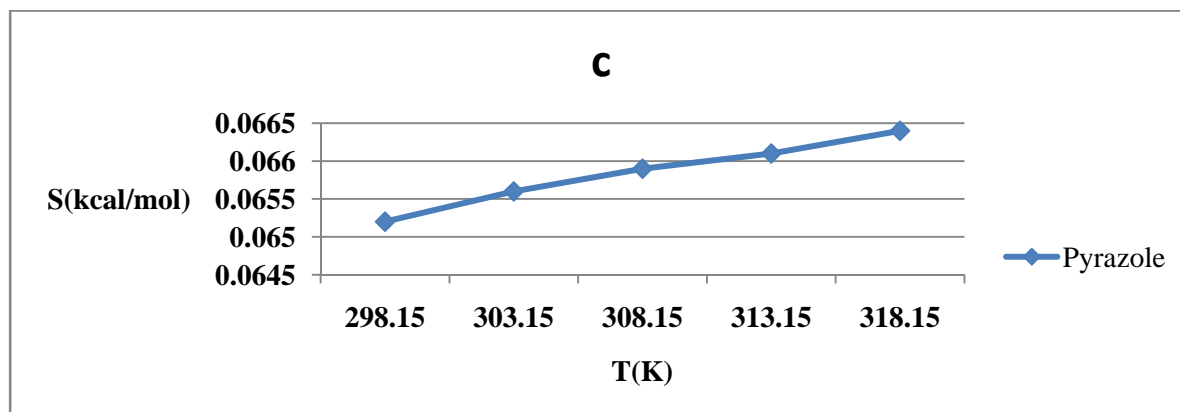| T(K)	H(kcalmol^{-1})	G(kcalmol^{-1})	S(kcalmol^{-1}k^{-1})
298.15	-141947.626	-141967.065	0.0652
303.15	-141947.616	-141967.502	0.0656
308.15	-141947.606	-141967.913	0.0659
313.15	-141947.596	-141968.295	0.0661
318.15	-141947.586	-141968.711	0.0664
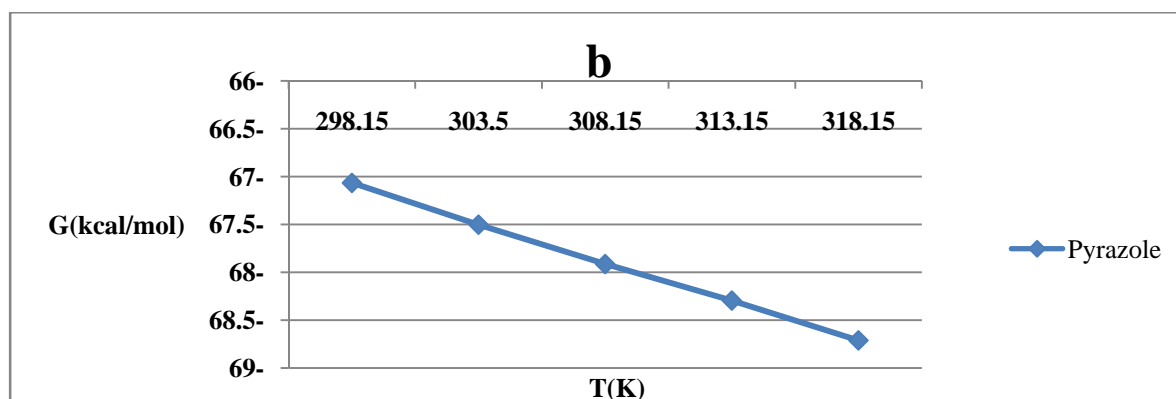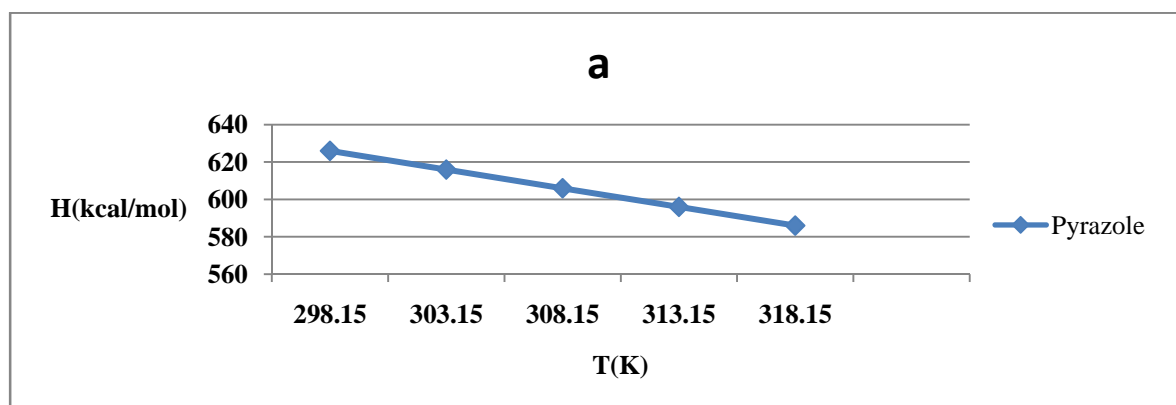
Fig. 1. Plots of the Enthalpy H(in kcal mol^{-1}) of versus temperature (K)(a), Gibbs free energies G (in kcal mol^{-1}) versus temperature (K)(b), Entropy S (in kcal mol^{-1}) versus temperature (K)(c),of Pyrazole.

CONCLUSIONS

The thermodynamic analysis shows with the increase of temperature, the Gibbs free energy of Pyrazole decreases and the enthalpy and entropy of Pyrazole increases. This means that with increase of temperature, the stability of Pyrazole increases.

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