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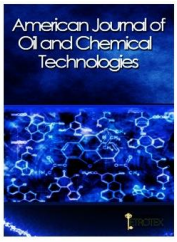

Study of synthesis of 1-(4-nitrophenyl)-1H-tetrazole from the reaction of 4-(dihydroxyamino) benzonitrile with Sodium azide in different temperature conditions, the DFT method

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Abstract:

In this article, synthesis of 1-(4-nitrophenyl)-1H-tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide in different conditions of temperature, with density functional theory method were studied. For this purpose, at first the material contained in the both sides of reaction were geometrically optimized, then the calculation of the thermodynamic parameters performed on all of them. The amount of ΔH, ΔS and ΔG of this reaction at different temperatures in form of sum of parameters discrepancy in the products than reactants is obtained. And finally, the best temperature for the synthesis of explosive according to the obtained thermodynamic parameters were evaluated.

Keyword: 1-(4-nitrophenyl)-1H-tetrazole, synthesis , 4- (dihydroxyamino) benzonitrile , Sodium azide

1. Introduction

The first Tetrazole was built in 1885 by Swedish chemists. In fact, the first Tetrazole was synthesized with name 2-phenyl-H2-Tetrazole-5-Carbonitril. Later this combination was used for the synthesis of non-substituted Tetrazole . In recent years, new energetic materials considered and due to the special properties, have many applications in the military field. Currently many researchers around the world with high density based on energetic materials such as Tetrazole doing research, this energetic materials in the production of pyrotechnics with less smoke, gas generators and engines are widely used and also less sensitive to heat and shock of their show. Another benefit of this combination compared to conventional energetic substances, they are green. Because these reactions were less environmental hazard and let it show better performance. Energetic materials commonly used fossil that often have high carbon content. During the process of burning large amounts of carbon dioxide (CO_2), carbon monoxide (CO) and unburned carbon particles such as soot produce and environmental pollutants and pollution and create a lot of problems. Nitrogen-rich compounds widely used in propulsion systems, fire extinguishing systems and airbag systems as well as fuel for missiles and military systems. In this study, the synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4- (hydroxy acids D) Benzo nitril is studied with Sodium Azide under different conditions of temperature, density functional theory method. Some chemical properties calculated in the level of B3lyp / 6-31g for 1-(4-nitrophenyl)-1H-tetrazole is shown Table 1.

Table 1. Some chemical properties calculated in B3lyp / 6-31g to Material 1- (4-nitrophenyl) -1 hydrogen Tetrazole.

	Temperature=298.15K , pressure=1 atm
	1- (4-nitro-phenyl) hydrogen 1. Tetrazole
	$C_7H_5N_5O_2$
ENERGY(au)	-693.803634
E HOMO(eV)	-3.04
E LUMO (eV)	-0.59
Dipole Moment (debye)	2.42
Weight(amu)	191.150
Volume(A^3)	166.13
Area (A^2)	189.26
Polarizibility	53.71
ZPE (KJ/mol)	342.27
H° (au)	-693.663336
CV (J/mol)	162.43
S° (J/mol)	395.58
G° (au)	-693.708257

2. Calculations and Results

Reviews the calculation of the synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide, under different conditions of temperature, studied by density functional theory, the operation was performed using the software Gaussian 98 and Gaussian view. First, compounds were optimized in a series of basic using density functional theory (6-31g) and then IR studies are done in order to calculate thermodynamic parameters of the process. All calculations are done in the level B3lyp / 6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure, the Studied reaction is:

$$C_7H_4N_2O_2+1/2H_2+N_3^- \rightarrow C_7H_5N_5O_2 \qquad (1)$$

1.2. Calculate and verify the values of changes in enthalpy (ΔH)

By using Gaussian 98 program were calculated enthalpy values for raw materials and products in process synthesis. For calculating and obtain the change in enthalpy in the reaction A + B → AB from the following formula is used:
Equation 1):

$$\Delta H=H_{product} - H_{reactant} \qquad (2)$$

With regards to reaction(1), Enthalpy values obtained through calculation software Gaussian, is as follows:

$$\Delta H_f = [H_{C7H5N5O2}]-[1/2H_{H2}+ H_{N3^-} + H_{C7H4N2O2}] \qquad (3)$$

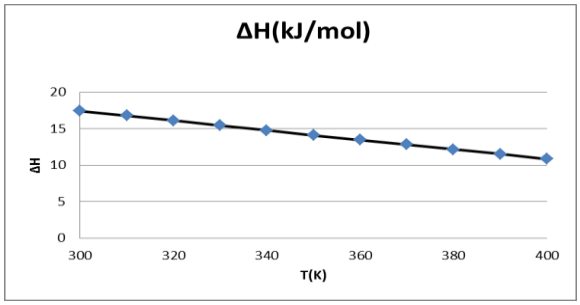

Figure 1. Diagram of the enthalpy changes for the synthesis material 1- (4-nitrophenyl) -1 hydrogen Tetrazole at different temperatures.

Values of ΔHf are indicating that in synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide under different conditions of temperature, ΔH_f are decreased by increasing the reaction temperature (Figure 1).

2.2. Calculate and assess the values of change in entropy (ΔS)

By using Gaussian 98 program were calculated entropy values for reactants and products in process synthesis. For calculating and obtain the change in entropy in the reaction A + B → AB from the following formula is used:

$$\Delta S_{AB} = [S_{AB}] - [S_A + S_B] \qquad (4)$$

With regards to reaction 1, Entropy values obtained through calculation software Gaussian, is as follows:

$$\Delta S_f = [S_{C7H5N5O2}] - [1/2 S_{H2} + S_{N3^-} + S_{C7H4N2O2}] \qquad (5)$$

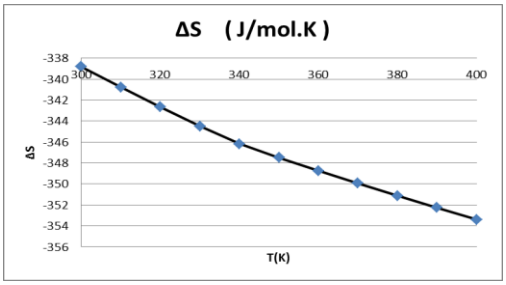

Figure 2. Diagram of the entropy changes for the synthesis material 1- (4-nitrophenyl) -1 hydrogen Tetrazole at different temperatures.

Values of ΔS_f are indicating that in synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide under different conditions of temperature, entropy changes have negative values, and are decreased by increasing the reaction temperature (Figure 2).

3.2. Calculate and verify specific heat capacity (CV)

By using Gaussian 98 program were calculated the specific heat capacity CV values for reactants and products in process synthesis.

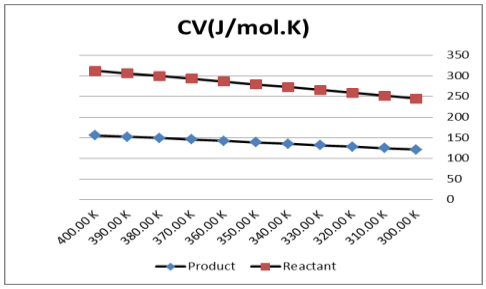

Figure 3. Diagram of the Specific heat capacity change (**C_V**) for the synthesis reaction of material 1- (4-nitro-

phenyl) -1 hydrogen Tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide at different temperatures.

Values of the specific heat capacity CV in product material 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4- (dihydroxyamino) benzonitrile with Sodium azide at different temperatures indicates that the product have specific heat capacity CV values, less than the reactant in the same conditions (Figure 3).

4.2. Calculate and verify the values of Gibbs free energy (ΔG)

By using Gaussian 98 program were calculated the values of Gibbs free energy (ΔG) for reactants and products in process synthesis. For calculating and obtain the change in values of Gibbs free energy (ΔG) in the reaction A + B → AB from the following formula is used:

$$\Delta G_{AB} = [G_{AB}] - [G_A + G_B] \qquad (6)$$

With regards to reaction1, The values of Gibbs free energy obtained through calculation software Gaussian, is as follows:

$$\Delta G_f = [G_{C7H5N5O2}] - [1/2G_{H2} + G_{N3^-} + G_{C7H4N2O2}] \qquad (7)$$

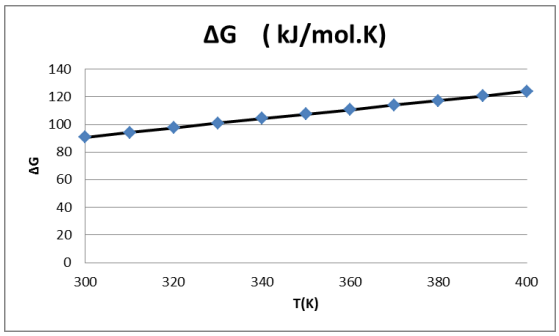

Figure 4. Diagram of Gibbs free energy changes (**ΔG_f**) for the synthesis reaction of material 1- (4-nitrophenyl) -1 hydrogen Tetrazole at different temperatures.

Values of ΔG_f indicates that the synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4-(dihydroxyamino) benzonitrile with Sodium azide under different conditions of temperature are positive, so the reaction be not spontaneous and with increasing temperature, the Gibbs free energy changes are more positive, so the reaction is best done at lower temperatures (Figure 4).

3. Discussion and conclusion

Results of the calculation for synthesis of 1- (4-nitrophenyl) -1 hydrogen Tetrazole from the reaction of 4-(dihydroxyamino) benzonitrile with Sodium azide under different conditions of temperature, is shown that ΔH_f at all temperatures are positive. It represents the endothermic nature of this process, which indicated heat absorbed, and ΔH_f are decreased by increasing the reaction temperature, so The reaction product contains more energy, also The lower specific heat capacity in the reaction product than the main reactant, show that the main product of the reaction is more energetic than the raw material. On the other hand values of Gibbs free energy (ΔG_f) indicates that this process is not done at different temperatures for spontaneous and with increasing temperature the Gibbs free energy changes more positive, so the reaction is best done at lower temperatures.

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