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The Synthesis of 2, 6 diamino- 3, 5-dinitropyridine from Direct Nitration Reaction of 2, 6 diamino pyridine in Different Temperature Conditions by Density Functional Theory

Neda Hajizadeh*

Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University, Tehran, Iran

*Corresponding author Fax number: Tel.: +98 9358778448

*E-mail: nedahajizadeh83@gmail.com

ABSTRACT

In this article, synthesis of the explosive 2, 6 (diamino) 3, 5 dinitro pyridine (ANPY) of the direct nitration reaction of 2, 6 diamino pyridine 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.

Keywords: Explosives, ANPY, synthesis, 2, 6 diamino 3, 5 – dinitro pyridine, nitration reaction

Introduction

Nitrogenous high-energy materials are semi-stable molecules with highly active, Their heat of formation is usually positive, the more thermodynamic materials have a more positive heat formation, they are the more unstable, As a result, they are more active These materials can be decomposed into smaller and more stable molecules and create high energy. Occasionally, the release of tensile energy from pressure rings is a source of energy release and explosion. Nitrogen-rich compounds are a bunch of high-energy compounds which are widely appreciated due to their high nitrogen content. The main product of the combustion process is nitrogen gas (N2) which is the most abundant gas in the Earth's atmosphere hence, there is no environmental pollution problem with the use of these compounds. The high-energy fossil materials that are commonly used often contain high carbon content, during the burning process, produce a large amount of carbon dioxide (CO2), carbon monoxide (CO) and carbon-free particles of carbon, such as soot which pollute the environment and cause pollution and many problems. Nitrogen-rich compounds in propulsion systems, fire extinguishing systems and airbag systems, as well as missile and military fuel systems, have been widely used.

In this research, the direct nitrate reaction of 2, 6 diamino pyridine has been studied under different temperature conditions for the synthesis of 2, 6 (diamino) 3, 5 di-nitro pyridine (ANPY) by density functional theory.

Calculations and results

Investigation of the synthesis of explosives 2 and 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) from the direct nitration reaction of 2, 6 diamino pyridine ($C_5H_7N_3$) became under different temperature conditions and using the functional density theory method, using Gaussian 98 and Gossive software. The compounds were initially optimized by the density functional theory method in the base series (6-31g), then, IR studies have been done to calculate the thermodynamic parameters of nitrite adsorption, all calculations were carried out at B3lyp / 6-31g levels at a temperature of 300 to 400 degrees Celsius and atmospheric pressure [1-3]. This reaction is:

$$C_5H_7N_3+2HNO_3 \rightarrow C_5H_5N_5O_4+2\ H_2O \qquad \text{equation 1}$$

Calculate and check the values of enthalpy changes

Using the Gaussian 98 program, the enthalpy values for raw materials and products were calculated in the synthesis process. The following equation is used to calculate and obtain enthalpy changes in the reactions A + B → AB [4].

$\Delta Hf = H_{products} - H_{reactants}$ equation 2

According to the reaction:

$C_5H_7N_3 + 2HNO_3 \rightarrow C_5H_5N_5O_4 + 2H_2O$ equation 3

The amount of enthalpy formed by calculating Gaussian software is as follows:

$\Delta H_f = [H_{C5H5N5O4} + 2H_{H2O}] - [H_{C5H7N3} + 2H_{HNO3}]$ equation 4

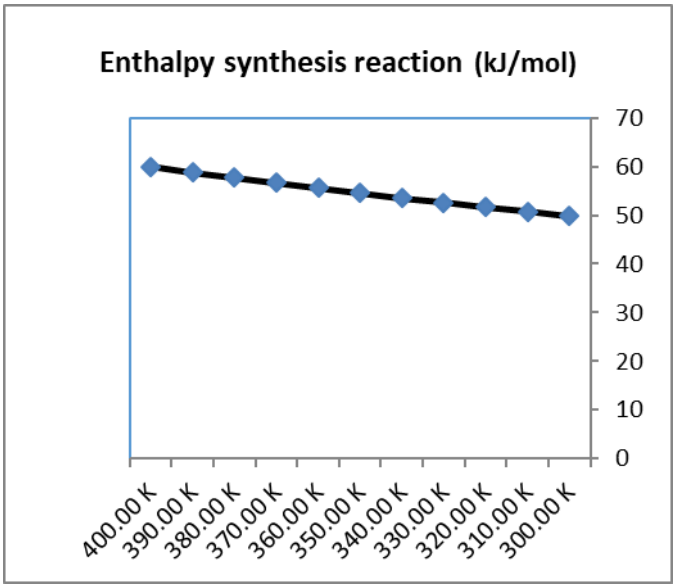

Figure 1. Shows the formation of enthalpy changes for synthesis of 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) at various temperatures

The value of ΔH_f indicates process of synthesis 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) is heated at different temperatures and with increasing reaction temperature the amount of enthalpy changes is positive [5, 6].

Calculating and evaluating entropy changes

The entropy values for raw materials and products were evaluated using the Gaussian 98 program in the synthesis process [7]. The following equation is used to calculate and obtain entropy variations in the reactions of A + B → AB.

$\Delta S_{AB} = [S_{AB}] - [S_A + S_B]$ equation 5

According to the reaction:

$C_5H_7N_3 + 2HNO_3 \rightarrow C_5H_5N_5O_4 + 2H_2o$ equation 6

The entropy values formed by computing the Gaussian software are as follows

$\Delta S_f = [S_{C5H5N5O4} + 2S_{H2O}] - [S_{C5H7N3} + 2 S_{HNO3}]$ equation 7

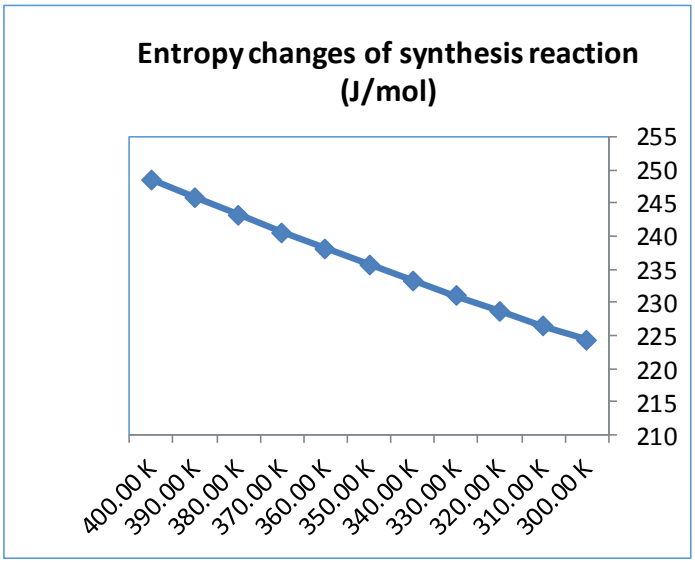

Figure 2. Shows the formation of entropy changes for synthesis of 2 and 6 (diamino) 3 and 5 di nitro pyridine ($C_5H_5N_5O_4$) at various temperatures

Calculate and test the specific heat capacity of the CV

Using the Gaussian program 98, the specific CV heat capacity values for raw materials and products were calculated in the synthesis process.

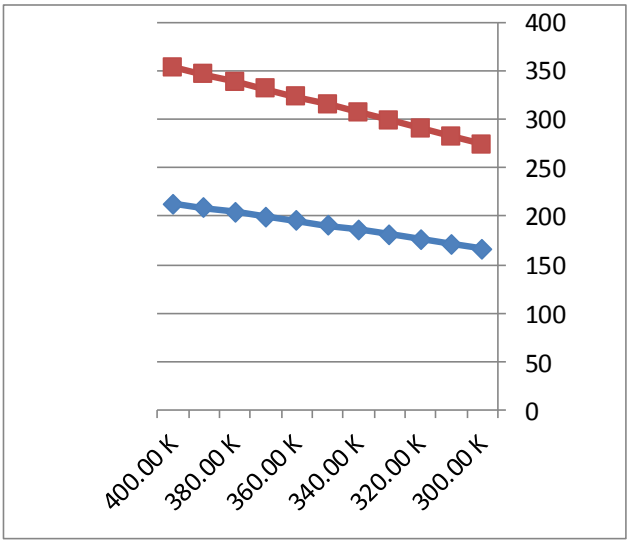

Figure 3. Shows the variation of the specific CV heat capacity variations in products 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) and the primary substance 2, 6 diamino pyridine ($C_5H_7N_3$) at various temperatures

The values of changes in the specific CV heat capacity in product 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) and the primary substance 2, 6 diamino pyridine ($C_5H_7N_3$) at different temperatures indicate that the product has a lower CV, In other words, under the same conditions, the temperature is increased by less heat than the raw material (Fig. 3) [8, 9].

Calculating and verifying the values of Gibbs free energy changes (ΔG)

Using the Gaussian program 98, Gibbs free energy (ΔG) was calculated for raw materials and products in the synthesis process. To calculate and obtain Gibbs free energy variations (ΔG), in the reactions A + B → AB, we use the following equation [10].

$$\Delta G_{AB} = [G_{AB}] - [G_A + G_B] \qquad \text{equation8}$$

According to the reaction:

$$C_5H_7N_3 + 2HNO_3 \rightarrow C_5H_5N_5O_4 + 2\,H_2O \qquad \text{equation 9}$$

The Gibbs free energy generated by calculating Gaussian software is as follows:

$$\Delta G_f = [G_{C5H5N5O4} + 2G_{H2O}] - [G_{C5H7N3} + 2\,G_{HNO3}] \qquad \text{equation 10}$$

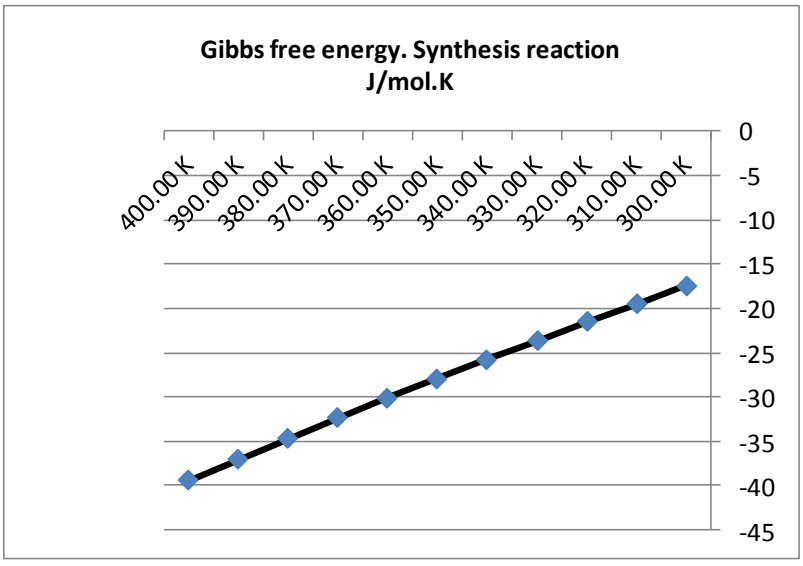

Figure 4. Shows the diagram of formation of ΔG_f for synthesis of 2 and 6 (diamino) 3 and 5 di nitro pyridine ($C_5H_5N_5O_4$) at various temperatures

The values of ΔG_f show that the process of synthesis 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) can be carried out at different temperatures independently And with increasing

temperature, the Gibbs free energy changes become more negative, so the reaction is better at higher temperatures (Fig.4)[11,12].

Discussion and conclusion

The results of the calculations show that in the process of synthesis 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) is heated at different temperatures and with increasing reaction temperature the amount of enthalpy changes becomes more positive and the degree of irregularity has increased. Changes in the specific heat capacity of CV in the 2, 6 (diamino) 3, 5 di nitro pyridine ($C_5H_5N_5O_4$) and the primary substance 2, 6 diamino pyridine ($C_5H_7N_3$) at different temperatures indicate the product has fewer CV-specific heat capacity values, which means that under the same conditions, the heat is reduced to less heat than the raw material. This suggests a much more energetic product than its primary material. The values of ΔG_f also indicate that this process can be carried out at different temperatures independently. As the temperature increases, Gibbs free energy changes, so the reaction is better at higher temperatures.

References

[1] T. G. Fox, P. J. Flory, *J. Appl. Phys.*, 21, 581, (1950).

[2] M. R. Jalali Sarvestani, R. Ahmadi, *Int. J. New. Chem.*, 4, 400-408, (2018).

[3] G. J. Price, *polymer.*, 31, 1745 (1990).

[4] R. Kavlock, K. Boekelheide, R. Chapin, M. Cunningham, E. Faustman, P. Foster, M. Golub, P.Williams, T. Zacharewski, *Reprod. Toxicol.*, 16, 721 (2002).

[5] M. R. Jalali Sarvestani, R. Ahmadi, *Int. J. New. Chem.*, 5, 409 (2018).

[6] W.Rodolf, S. Johnson, New Encyclopedia Britannica, *Micropaedia*, 1, 247 (1974).

[7] W. Jackson, M. Norman, *J. Chem. Soc.*,12, 268 (1969).

[8] M. Gordon, T. Wolfhesin, *Research and Engineering Company*, G.B. Patent, 1338778, (1973).

[9] R. Heinz, P. Theodor, Hoechst AG Company, *U.S. Patent*, 4719304, (1988).

[10] G. Johnson, M.R. Pavia, G. Johnson, Warner Lambert Company, *U.S. Patent*, 4826860, (1989).

[11] P. Rocío, C. Javier, C. Clementina, R. Julieta, *Bioorg. Med. Chem. Letters*, 15 (5), 1417 (2005).

[12] A. Rana, N. Siddiqui, A.Khansuroor, *Eur. J. Med. Chem.*, 43 (2), 173 (2008).

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