International Journal of New Chemistry, 2018, 5 (3), 91-102 .
Published online March 2018 in http://www.ijnc.ir ./
Original Article.

Online ISSN 2383-188X
Open Access

Original Article.

Evaluating the Thermodynamic Parameters the Derivative [b-5,1] tetrazolo [4,2,1] teriazine (TTA) with Boron nitride nano-cage in Different Temperature Conditions by DFT Method

***Masoumeh Jafari**

[1]*Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre-rey Branch, Islamic Azad University*

*Corresponding author Fax number: Tel.: +98 9127965471

*E-mail: masomeh.jafari2020@yahoo.com

ABSTRACT

In this research, the formed reaction derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Burnitride cage Nano-structure was studied in different temperature conditions by DFT method.

For this purpose, first, the materials on both sides of the reaction were the geometric optimization, then, calculation related to the thermodynamic parameters were done on all them. Then, the values of ΔS, ΔH and ΔG of this reaction at different temperatures are obtained by the difference in the sum of these parameters in the products to the primary materials and in the final, the best temperature for the synthesis of the explosive material derivative was evaluated according to the resulting thermodynamic parameters

Keywords: formed ΔH, matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA), Burnitride cage

---

Introduction

The Tetrazoles are ring and aromatic compounds with 4 nitrogen atom and carbon atom that applicable in military industries. These compounds release to the large amounts of gas N_2 through burning. So, they have little pollution for the environment and they are except from green explosives materials[1-2]. Today, many scientists around the world are researching on the full energy materials with high density based on Tetrazoles, environmental hazards of these compounds are lower relative to the fossil full energy materials that are commonly used and have high carbon content. Because, fossil fuels produce many soot at during the process of burning gases CO_2 , CO , and unburned carbon particles like that there are in the environment pollution and many problems.These nitrogen-rich compounds have been used in different industries. In this research, synthesis derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Burnitride cage has been studied temperature conditions by DFT method [3-5].

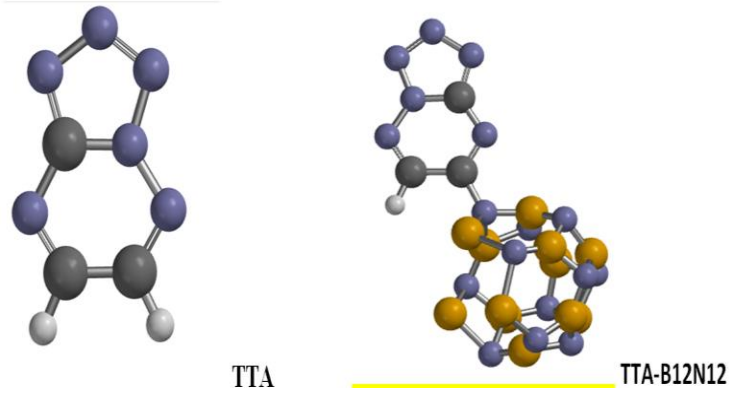
Table (1). Some chemical properties calculated in the level $B_3LYP/(6\text{-}31g)$ for matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) and its derivative with the Burnitride cage.

	Temperature=298.15K , pressure=1 atm	
	TTA	TTA-B12N12
ENERGY(au)	-435.171624	-1145.11262
E HOMO(eV)	-8.97	-4.42
E LUMO (eV)	3.39	1.02
Dipole Moment (debye)	5.97	3.01
Weight(amu)	122.091	404.892
Volume(A^3)	100.17	327.08
Area (A^2)	120.73	289.18
ZPE (KJ/mol)	204.48	540.31
H° (au)	-435.637672	-1318.70204
CV (J/mol)	80.58	312.28
S° (J/mol)	316.68	523.12
G° (au)	-435.673634	-1318.76145

1-Calculation and resulte

Computational review of synthesis derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Burnitride cage has been studied in different temperature conditions by DFT method. this operation was done with using of the Gaussian 98, Gausswave and Spartan software.

First, the compounds were optimized with DFT method in the base series (6-31g), then, studies IR was done to calculate thermodynamic parameters related to the process. All calculation in level B_3LYP/(6-31g) was done at a temperature of (300 to 400 Kelvin degrees) and one atmospheric pressure. The reaction reviewed case as follows[6-10].;



Figure(1). Optimized images of molecules of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) and its derivative with the Burnitride cage.

2-Calculation and results

Computational review of the formed reaction derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage has been studied in different conditions of temperature by DFT method. this operation was done with using of the Gaussian 98, Gausswave and Spartan software.

First, the compounds were optimized with DFT method in the base series (6-31g), then, studies IR were done for the calculate thermodynamic parameters related to the process. All calculation at level B_3LYP (6-31g) were carried out at a temperature of (300 to 400 Kelvin degrees) and one atomospheric pressure [11-14].

The reaction reviewed case as follows:

$$\mathbf{TTA + B_{12}N_{12} \rightarrow TTA\ B_{12}N_{12} + 1/2H_2} \qquad \mathbf{(1)}$$

Calculate and review the amounts of ΔH changes:

The ΔH amounts were calculated for primary materials and products in the synthesis process. For the calculation and obtaining of ΔH changes in reactions A+B→C+D from the following equation is used:

$$\Delta H_f = \Sigma H_{Products} - \Sigma H_{Reactants} \quad (2)$$

Now with regard to the reaction:

$$TTA + B_{12}N_{12} \rightarrow TTA\ B_{12}N_{12} + 1/2H_2$$

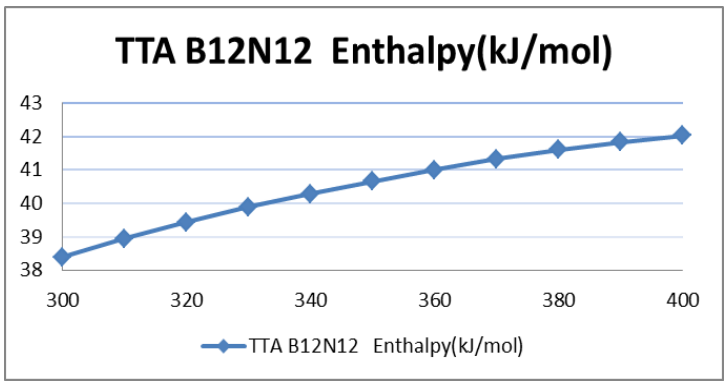
The formed ΔH amounts obtained by calculation Spartan software are as follow:

$$\Delta H_f = [H_{TTA\ B12N12} + 1/2H_{H2}] - [H_{TTA} + H_{B12N12}] \quad (3)$$

Table(2). The formed ΔH calculated in level B_3LYP (6-31g) for derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage

	Enthalpy(kJ/mol)
Temperature	TTA B12N12
300	38.3934
310	38.9438
320	39.43345
330	39.8884
340	40.28725
350	40.65725
360	40.9992
370	41.3137
380	41.5909
390	41.82095
400	42.02545

The formed ΔH calculated in level B_3LYP (6-31g) for derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage, always in all temperature range 300 to 400 Kelvin degrees has been positive.



Figure(2). The formed ΔH changes diagram for synthesis derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage at different temperatures.

The value ΔH_f is positive that shows, the synthesis process derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage at different temperatures from 300 to 400 Kelvin degrees is warm-up and with increasing reaction temperature the amount of released heat is reduced..figure(2)

Calculate and review the amount of ΔS changes;

The results of the calculations show that ΔS amounts for primary materials and products in the synthesis process were calculated. For the calculation and obtaining of ΔS changes in reactions A+B→C+D the following equation is used;

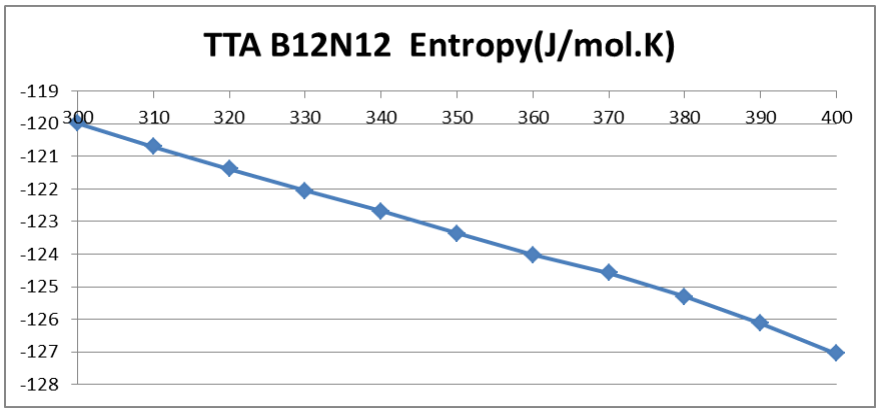
$$\Delta S_f = \Sigma S_{Products} - \Sigma S_{Reactants} \quad (4)$$

Now with regard to the reaction;

$$TTA + B_{12}N_{12} \rightarrow TTA\ B_{12}N_{12} + 1/2H_2$$

The formed ΔS amounts obtained by calculating Gaussian software are as follows;

$$\Delta S_f = [S_{TTA\ B12N12} + 1/2S_{H2}] - [S_{TTA} + S_{B12N12}] \quad (5)$$



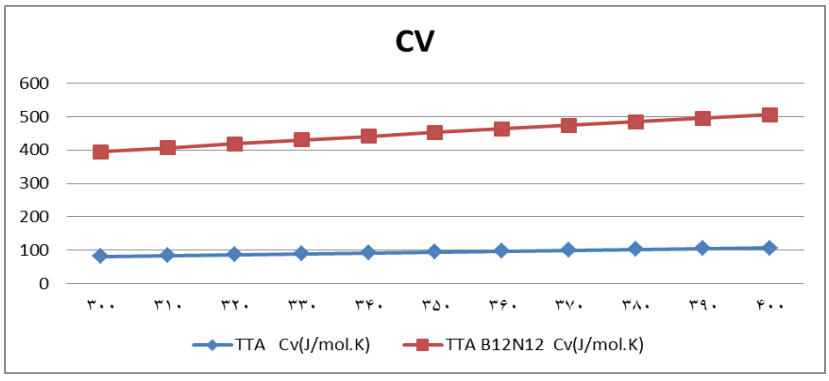
Figure(3). The formed ΔS changes diagram for synthesis derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage at different temperatures

The positive value ΔS_f is show that synthesis process derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage at different temperatures has an entropy negative. Figure(3)

Calculate and review special heat capacity (C_v);

The results of the calculation show that special heat capacity amounts (C_v) for primary materials and products in the synthesis process were calculated that shows the following process.

$B_{12}N_{12}$ TTA > TTA (6)



Figure(4). The special heat capacity (C_v) changes diagram in primary materials and matter [b-5,1] Tetrazolo [4,2,1] teriazine (TTA) and its derivative with the burnitride cage at different temperatures.

Table(3). the special heat capacity calculated in level B_3LYP (6-31g) for primary material and matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) and its derivative with the Burnitride cage at different temperatures.

	Cv(J/mol.K)	
Temperature	TTA	TTA B12N12
300	81.081	313.9806
310	83.7797	323.0873
320	86.4696	332.0586
330	89.1469	340.892
340	91.8081	349.5856
350	94.4501	358.1378
360	97.0699	366.5477
370	99.6648	374.8142
380	102.2322	382.937
390	104.77	390.9157
400	107.276	398.7502

The special heat capacity(C_v) changes amounts for primary materials and matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) and its derivative with the Burnitride cage at different temperatures, it show that the product has a more specific heat capacity (C_v), that is, in the same conditions its increases temperature with getting more heat relative to the primary material. Figure(4)

Calculate and review the amounts of Gibbs free energy changes (ΔG):

The results of the calculation show that the Gibbs free energy amounts (ΔG) for primary materials and products in the synthesis process were calculated. For the calculation and obtaining

of Gibbs free energy changes (ΔG) in reactions A+B→C+D from the following equation is used:

$$\Delta G_f = \Sigma G_{Products} - \Sigma G_{Reactants} \quad (7)$$

Now with regard to the reaction

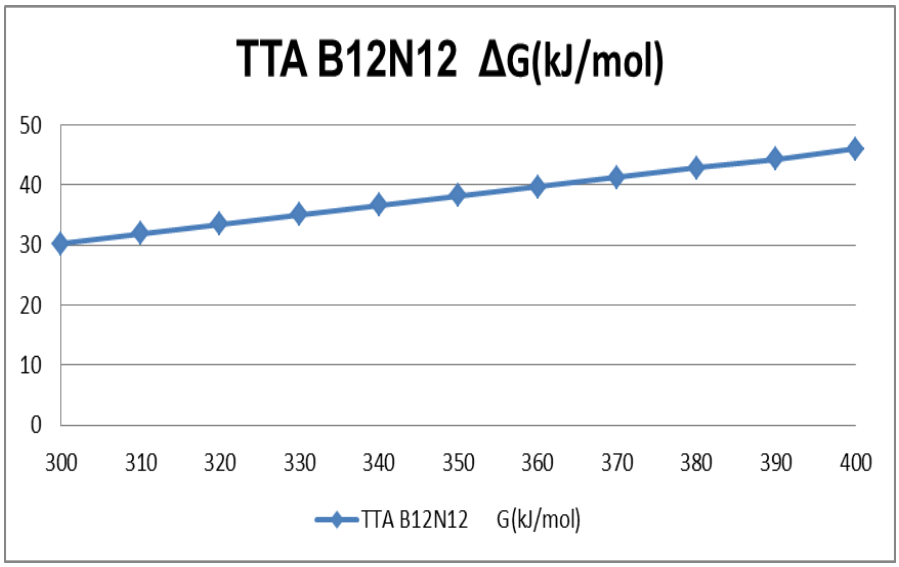
$$TTA + B_{12}N_{12} \rightarrow TTA\ B_{12}N_{12} + 1/2H_2$$

The formed Gibbs free energy amounts obtained by calculating Gaussian software are as folloes:

$$\Delta G_f = [G_{TTA\ B12N12} + 1/2G_{H2}] - [G_{TTA} + G_{B12N12}] \quad (8)$$

Table(4). The formed Gibbs free energy calculated in level B_3LYP (6-31g) for primary material and matter [b-5,1] Tetrazolo [4,2,1] teriazine (TTA) and its derivative with the burnitride cage at different temperatures.

	G(kJ/mol)
Temperature	TTA B12N12
300	30.2786
310	31.9207
320	33.52075
330	35.1083
340	36.64855
350	38.20955
360	39.75735
370	41.26555
380	42.8228
390	44.3881
400	46.0004



Figure(5). The formed Gibbs free energy values (ΔG_f) diagram for synthesis derivative of matter [b-5,1] Tetrazolo [4,2,1] teriazine (TTA) with Nano structure Burnitride cage at different temperatures.

The negative values (ΔG_f) is show that the synthesis process derivative of matter [b-5,1] Tetrazolo [4,2,1] teriazine (TTA) with Nano structure Burnitride cage at different temperatures, it's not spontaneous and with temperature increases, Gibbs free energy become more positive. So, the reaction at high temperatures is done lower.figure(5) [15-17].

Results and discussion:

The results of the calculation show that in the synthesis process derivative of matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) with Nano structure Burnitride cage at different temperatures, the value ΔH_f in all temperatures is positive that shows warm-up this process and with increasing reaction temperature the amount of released heat is decreased.

Whatever the thermodynamic materials have more positive formed heat, more unstable and in result are more active. Nitrogenous full-energy material, semi-stable molecules are with high activity, that their formed heat is positive and obviously these materials degrade to the smaller and more stable molecules and from them are produced high energy. Some times, the release of tensile energy related to under pressure rings is the cause of energy release and explosion. On the

other the formed process has an entropy (ΔS) negative and with temperature increasing,ΔS has .decreased

Conclusion

The specific heat capacity (C_v) changes is show specific heat capacity for primary material and matter [b-5,1] Tetrazolo [4,2,1] Teriazine (TTA) related to its derivative with the Burnitride cage at different temperatures has lower values. That is, in the same conditions its increases . temperature with getting less heat relative to the products

The lower specific heat (C_v) represents full-energy of material TTA is related to its derivative, on the other, Gibbs free energy changes values (ΔG_f) shows that the mention process at different temperatures calculated 300 to 400 Kelvin degrees it's not be done spontaneous and with temperature increases, Gibbs free energy changes become more positive. So, the reaction at more temperatures is done lower

[1] N. Maddah Zadeh Darini, R. Ahmadi, *Int. J. New. Chem.*, 2, 228 (2015).

[2] R. Ghiasi, R. Ahmadi, *Int. J. New. Chem.*, 1, 30 (2014).

[3] R. Ahmadi, M. R. Jalali Sarvestani, B. Sadeghi, *Int. J. Nano. Dimens.*, 9, 325-335.

[4] M. R. Jalali Sarvestani, T. Boroushaki, M. Ezzati, *Int. J. New. Chem.*, 5, 428 (2018).

[5] R. Ahmadi, M. Ebrahimikia, *Phys. Chem. Res.*, 5, 617 (2017).

[6] M. Ezzati, R. Ahmadi, T. Boroushaki, E. S. Mirkamali, B. Farhang, *Int. J. New. Chem.*, 5, 435 (2018).

[7] H. Ono, and K. Koyanagi, Appl. Phys.Lett., 77, 1431 (2000).

[8] Min Fu, Yalin Li, Siwei wu, Peng Lu, Jing Liu, Fan Dong, Appl. Surf. Sci., 258, 15857 (2011).

[9] H. Fu, C. Pan, W. Yao, Y. Zhu, J. Phys.Chem. B., 109, 22432 (2005).

[10] K. Vignesh, A. Suganthi , M. Rajarajan,S.A. Sara, Powder Technol., 224, 331 (2012).

[11] C. Karunakaran, A. Vijayabalan, and G.Manikandan, Superlattices Microstruct., 51, 443 (2012).

[12] R. H. Rosalie, K. H. Takuya Tsuzuki, Mater. Chem. and Phys., 132, 1035 (2012).

[13] N. Upadhayay, Chem. Sci. Trans., 2(2),455, (2013).

[14] A. Tomkiewicz, J. Kłak, J. Mroziński,Materials Science-Poland, 22, 3, (2004).

[15] R. J. Usha, J. A. M. Mani, V. Joseph,Archives of Appl. Sci. Res., 4(1), 638 (2012).

[16] M. Kooti, Z. Noori, J. Appl. Chem. Res.,4(14), 47, (2010).

[17] L. Dobrzañska, G. Wrzeszcz, A. Grodzicki,F. Rozpłoch, Polish J. Chem., 74, 1017 (2000).