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The synthesis of α,2,4,6-tetranitrotoluene from the reaction of 2,4,6-trinitrotoluene (TNT) with Fluorotrinitromethane in different temperature conditions, the DFT method

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Abstract:

In this article, synthesis of the α,2,4,6-tetranitrotoluene from the reaction of 2,4,6-trinitrotoluene (TNT) with Fluorotrinitromethane 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, and 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: DFT method, synthesis, 2,4,6-trinitrotoluene (TNT), Fluorotrinitromethane

1. Introduction

Trinitro Toluene or TNT or Trotil is a yellow crystalline compound which melts at 354 degrees Kelvin. TNT is explosive which detonation velocity of 7028 meters per second and used in many of the compounds explosives. TNT is prepared by nitration of toluene $C_6H_5CH_3$,its and that chemical formula is (CH_3 $(NO_2)_3$ C_6H_2) (Figure 1,2). In recent years, new energetic materials attention that due to the special properties, have many applications in the military field. TNT the first time in 1863 by a German chemist named Joseph Willebrand built, but the impact and its effects were not understood until many years later. Because it was more difficult to blow it up and another reason was that less explosive power. Generally, when it is processed with steam or hot water capability can be poured in boxes or in any form. German army from this material used to fill casings military in 1902. They use this material in World War I and used in submarines. They made pellets of which, could would pass of bulletproof walls of English Warship and ships. While the English bullets exploded as soon as collision with armored shell. In this study, the synthesis material tetra-nitro toluene from the reaction -α 6,4,2 tri nitro toluene 6.4.2 (TNT) is studied with more Fluoro nitro methane in different conditions of temperature, density functional theory method Table 1.

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Figure 1. Reaction Equation of synthesis of the α,2,4,6-tetranitrotoluene

Table 1. Some chemical properties calculated in B3lyp / 6-31g to Material α- 2,4,6 tri-nitro toluene (TNT) and Nitrotoluene

	Temperature=298.15K , pressure=1 atm	
	The main raw material	Main Product
	$C_7H_5N_3O_6$	$C_7H_4N_4O_8$
ENERGY	-868.580085 au	-1069.27121 au
ENERGY(aq)	-868.584232 au	-1069.27904 au
SOLVATION ENERGY	-10.89 kJ/mol	-20.55 kJ/mol
E HOMO	-8.06eV	-8.08 eV
E LUMO	3.29 eV	2.67 ev
Dipole Moment	1.11 debye	2.75 debye
weight	227.132 amu	272.129 amu
volume	184.25 A^3	207.25 A^3
Area	211.40 A^2	240.35 A^2
Polarizibility	53.65	55.66
ZPE	394.35 KJ/mol	396.16 KJ/mol
H°	-868.417679 au	-1069.10651 au
CV	198.13 J/mol	230.42 J/mol
S°	441.21 J/mol	471.99 J/mol
G°	-868.467782 au	-1069.16011 au

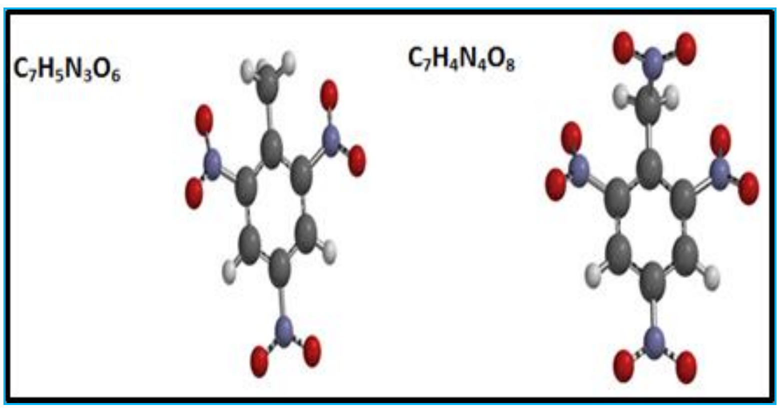

Figure 2. Optimized screenshots of molecules α,2,4,6-tetranitrotoluene (right) and 2,4,6-trinitrotoluene (TNT) (left)

2. Calculations and Results

Examine the calculation synthesis of α,2,4,6-tetranitrotoluene from the reaction of 2,4,6-trinitrotoluene (TNT) with Fluorotrinitromethane in different conditions of temperature were studied with more Fluoro nitro methan, with density functional theory methods. This operation was performed by using Gaussian 98 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. Studied the reaction is:

$$C_7H_5N_3O_6+FC(NO_2)_3\rightarrow C_7H_4N_4O_8+FC(NO_2)_2^-+1/2H_2 \quad (1)$$

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:

$$\Delta H_f = [H_{C7H4N4O8+} H_{C7H4N2O2+} 1/2H_{H2}] - [H_{C7H5N3O6+} H_{FC(NO2)3}] \qquad (3)$$

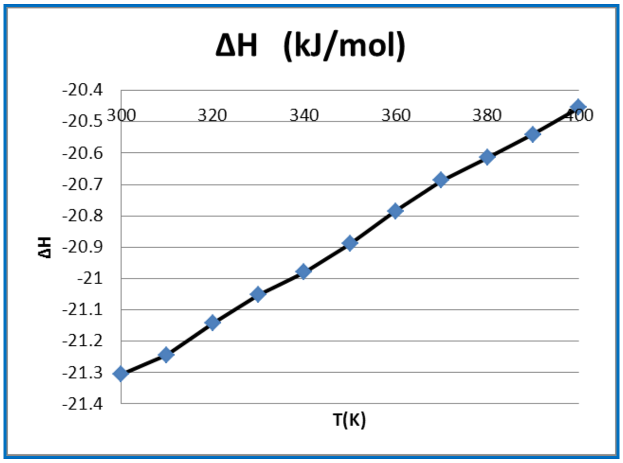

Figure 3. Diagram of the enthalpy changes for the synthesis α,2,4,6-tetranitrotoluene at different temperatures.

Value of ΔH_f is negative, indicating that the process of synthesis of tetra-nitro toluene from the reaction α-2,4,6-trinitrotoluene (TNT) with more Fluoro nitro methane at temperatures ranging from 300 to 400 K, inserts, heating and increasing the amount of heat released is less by the reaction temperature (Figure 3).

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:

$$\Delta S_f = [S_{C7H4N4O8+} S_{C7H4N2O2+} 1/2S_{H2}] - [S_{C7H5N3O6+} S_{FC(NO2)3}] \qquad (5)$$

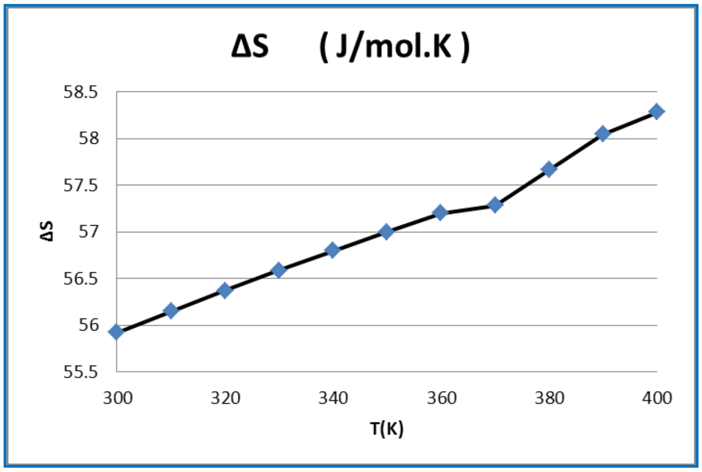

Figure 4. Diagram of the entropy changes for the synthesis α,2,4,6-tetranitrotoluene at different temperatures.

Value of ΔSf is positive indicates that the process of synthesis of tetra-nitro toluene from the reaction -α 6,4,2 tri nitro toluene 6.4.2 (TNT) with more Fluoro nitro methane at different temperatures have positive enthropy that with increasing temperature the irregularities Increased (Figure 4).

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.

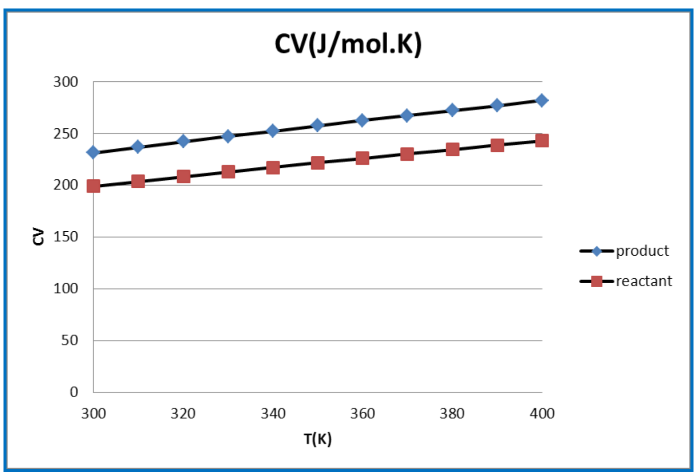

Figure 5. Diagram of the Specific heat capacity change (**C**$_V$) for molecules α,2,4,6-tetranitrotoluene and 2,4,6-trinitrotoluene (TNT) at different temperatures.

Values of the specific heat capacity CV in product material α,2,4,6-tetranitrotoluene from 2,4,6-trinitrotoluene (TNT) at different temperatures indicates that the main product have specific heat capacity CV values, less than main the reactant in the same conditions (Figure 5).

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:

$$\Delta G_f = [G_{C7H4N4O8} + G_{C7H4N2O2} + 1/2G_{H2}] - [G_{C7H5N3O6} + G_{FC(NO2)3}] \qquad (7)$$

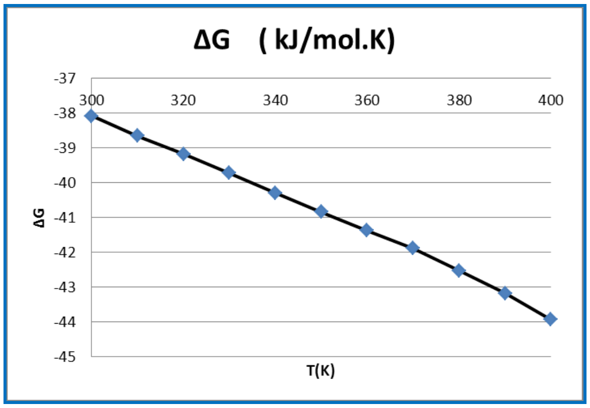

Figure 6. Diagram of Gibbs free energy changes (**ΔG_f**) for the synthesis reaction for the synthesis α,2,4,6-tetranitrotoluene at different temperatures .

Value of ΔG_f is negative indicate that the process of synthesis of α,2,4,6-tetranitrotoluene at different temperatures, to be done spontaneously and with Free Gibbs energy more negative temperatures rise, so the reaction is best done at higher temperatures (Figure 6).

3. Discussion and conclusion

Results of the calculation synthesis of α,2,4,6-tetranitrotoluene from the reaction of 2,4,6-trinitrotoluene (TNT) with Fluorotrinitromethane in different conditions of temperature, with density functional theory method were studied ΔH_f at all temperatures are negative. It represents the exothermic nature of this process. By increasing the amount of reaction temperature the heat released is lower. On the other hand it has positive entropy. With increasing temperature amount of entropy has increased. In other words, Amount of disorder has increased. Values of the specific heat capacity CV changes in product material -α 6,4,2 tetra nitro toluene and more raw material 6.4.2 Nitro Toluene (TNT) at different temperatures indicates that the product has specific heat capacity C_V values less the same conditions, the less heat than raw material increases its temperature. Represents the more energetic of the matter is the product of the raw material. On the other hand values of Gibbs liberalization energy (ΔG) indicates that the process is calculated at different temperatures 300 to 400 degrees Kelvin and that is done as spontaneous. Gibbs free energy becomes more negative with increasing temperature changes, therefore reaction at higher temperatures, done better.

4. References:

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