The synthesis of 5-picrylamino-1, 2, 3, 4-tetrazole (PAT) from the reaction of 5-amino-1, 2, 3, 4-tetrazole with picryl chloride in different temperature conditions, the DFT method

Neda Hajizadeh* and Azade Saadat

Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahr-e-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 synthesis of 5-picrylamino-1, 2, 3, 4-tetrazole (PAT) from the reaction of 5-amino-1, 2, 3, 4-tetrazole with picryl chloride 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: 5-picrylamino-1, 2, 3, 4-tetrazole (PAT), synthesis, 5-amino-1, 2, 3, 4-tetrazole, picryl chloride
Introduction

Many researchers are studying on the high-energy and high-tech materials based on tetrazole, these high-energy materials are widely used in the production of pyrotechnic materials with chimneys, gas generators and propulsion engines. They are also less sensitive to heat and shock and have many applications in the military field [1-10]. Tetrazoles are ring and aromatic compounds, which include four nitrogen atoms and one carbon. These compounds are widely used in various industries, including military industries. These compounds release large amounts of N₂ gas after combustion and that's why they have little pollution for the environment and are considered a green explosive [11-15]. By introducing tetrazoles in the structure of polymeric chains, the energetic properties of polymers can be increased. So far, various methods have been reported for the synthesis of poly tetrazoles, most of them tetrazoles are hanging and attached to the main chain. In the case of the use of functionalized tetrazole rings as monomers, the rings can be inserted into the main polymer chain structure. The environmental hazards of these compounds are lower than the high-energy fossil materials that are commonly used and have high carbon content that during the burning process generate large amounts of carbon dioxide and carbon monoxide and carbon-free carbon particles such as soot that create pollution and problems in the environment. Nitrogen-rich compounds are used in propulsion systems, fire extinguishing systems and airbag systems, as well as missile and military fuel systems. In this research, the synthesis of Article 5-Pyridine-1, 2, 3, 4-tetrazole (PAT) from the reaction of the 5-amino-1, 2, 3, 4-tetrazole with chloride picric acid under different temperature conditions was studied by density functional theory [16-21].
<table>
<thead>
<tr>
<th></th>
<th>Original material</th>
<th>Main product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{C}_6\text{H}_2\text{ClN}_3\text{O}_6 )</td>
<td>( \text{C}_7\text{H}_9\text{N}_6\text{O}_4 )</td>
</tr>
<tr>
<td>ENERGY</td>
<td>-1293.06017 au</td>
<td>-1145.11262 au</td>
</tr>
<tr>
<td>ENERGY(aq)</td>
<td>-1293.06073 au</td>
<td>-1145.12608 au</td>
</tr>
<tr>
<td>SOLVATION ENERGY</td>
<td>-1.48 kJ/mol</td>
<td>-35.33 kJ/mol</td>
</tr>
<tr>
<td>E HOMO</td>
<td>-11.88 eV</td>
<td>-10.72 eV</td>
</tr>
<tr>
<td>E LUMO</td>
<td>-0.61 eV</td>
<td>-0.62 eV</td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>0.29 debye</td>
<td>5.39 debye</td>
</tr>
<tr>
<td>weight</td>
<td>247.550 amu</td>
<td>296.159 amu</td>
</tr>
<tr>
<td>volume</td>
<td>175.80 ( \text{A}^3 )</td>
<td>215.73 ( \text{A}^3 )</td>
</tr>
<tr>
<td>Area</td>
<td>202.66 ( \text{A}^2 )</td>
<td>244.04 ( \text{A}^2 )</td>
</tr>
<tr>
<td>POLARIZABILITY</td>
<td>52.98</td>
<td>56.49</td>
</tr>
<tr>
<td>ZPE</td>
<td>268.96 KJ/mol</td>
<td>421.15 KJ/mol</td>
</tr>
<tr>
<td>( \text{H}^\circ )</td>
<td>-1292.94620 au</td>
<td>-1144.93837 au</td>
</tr>
<tr>
<td>CV</td>
<td>185.70 ( \text{J/mol} )</td>
<td>237.93 ( \text{J/mol} )</td>
</tr>
<tr>
<td>( \text{S}^\circ )</td>
<td>431.43 ( \text{J/mol} )</td>
<td>473.26 ( \text{J/mol} )</td>
</tr>
<tr>
<td>( \text{G}^\circ )</td>
<td>-1292.99519 au</td>
<td>-114499212 au</td>
</tr>
</tbody>
</table>

Table 1. Some chemical properties calculated at B3lyp / 6-31g levels for 5-picrilamino-1, 2, 3, 4-tetrazole (PAT) and 1 and 5 diaminoto-tetrazole (\( \text{CH}_4\text{N}_6 \)).
Calculations and results

Computational review of Synthesis of Article 5-Pyrrolamino-1, 2, 3, 4-tetrazole (PAT) from the reaction of the 5-amino-1, 2, 3, 4-tetrazole with chloride picrilic acid under different temperature conditions was studied by density functional theory, this operation was performed using Gaussian 98 and Gossive software [8]. The compounds were initially optimized by the density functional theory method in the base series (6-31g), IR studies calculate the thermodynamic parameters related to the process, all calculations were carried out at B3lyp / 6-31g levels at a temperature of 300 to 400 °K and atmospheric pressure [9]. This reaction is:

\[ C_6H_2ClN_3O_6+CN_3H_3 \rightarrow C_7H_4N_6O_6+ HC \]  

**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 [10]. The following equation is used to calculate and obtain enthalpy changes in the reactions \( A + B \rightarrow AB \) [11].

\[ \Delta H = H_{final} - H_{initial} \]  

**equation 2**

According to the reaction:

\[ C_6H_2ClN_3O_6+CN_3H_3 \rightarrow C_7H_4N_6O_6+ HCl \]  

**equation 3**

The values of enthalpy formation obtained by calculating Gaussian software are as follows:

\[ \Delta H_f = [H_{C_7H_4N_6O_6+ HCl}] - [H_{C_6H_2ClN_3O_6+ CN_3H_3}] \]  

**equation 4**
Figure 1. Shows the information diagram for the Synthesis of Article 5. -Pacyr Amino-1, 2, 3, 4-Tetrazole (PAT) from the reaction of substance 5 - Amino-1, 2, 3, 4-Tetrazole with chloride picril at different temperatures.

The amount of $\Delta H_f$ indicates that the process of synthesis of 5-picrolamino-1,2,3,4-tetrazole (PAT) from the reaction of the 5-amino-1,2,3,4-tetrazole reaction with chloride picril at different temperatures and with increasing temperature. The reaction temperature will increase the amount of heat released (Fig1).

Calculating and evaluating entropy changes

The entropy values for raw materials and products were evaluated using the Gaussian 98 program in the synthesis process [12-14]. To calculate and obtain entropy variations in the reactions $A + B \rightarrow AB$ [15], the following equation is used:

$$\Delta S_{AB} = [S_{AB}] - [S_A + S_B]$$  \hspace{1cm} \text{equation 5}

According to the reaction:

$$C_6H_2ClN_3O_6 + CN_3H_3 \rightarrow C_7H_4N_8O_6 + HCl$$  \hspace{1cm} \text{equation 6}

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

$$\Delta S_f = [S_{C_7H_4N_8O_6} + S_{\text{HCl}}] - [S_{C_6H_2ClN_3O_6} + S_{\text{CN}_3H_3}]$$  \hspace{1cm} \text{equation 7}
Fig. 2 shows the formation of entropy changes for synthesis of 2 and 6 (diamo) 3 and 5 di nitropyridine 
(C$_6$H$_3$N$_3$O$_4$) at various temperatures

The amount of ΔS$_f$ shows that the process of synthesis of matter-5-picrolamino-1, 2, 3, 4-
tetrazole (PAT) from the reaction of substance 5 - amino-1, 2, 3, 4-tetrazole with chloride 
picrilium has a negative entropy at different temperatures. Which, with increasing temperature, 
entropy becomes more negative (Fig. 2)

**Calculate and test the specific heat capacity**

Using the Gaussian program 98, the specific heat capacity values for raw materials and products 
were calculated in the synthesis process [16-18].

Figure 3: Specific heat capacity diagram in Article 5 - Amino-1, 2, 3, 4-tetrazole (PAT) and primary material 5-
Amino-1, 2, 3, 4-tetrazole at various temperatures
The values of changes in the specific heat capacity in Article 5, Amino-1, 2, 3, 4-tetrazole (PAT) and the primary substance 5-amino-1, 2, 3, 4-tetrazole at various temperatures indicate that the product of the heat capacity under the same conditions, the heat is raised by less heat than that of the heating element (Fig. 3).

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

Using the Gaussian program 98, Gibbs free energy was calculated for raw materials and products in the synthesis process [19-21]. To calculate and obtain Gibbs free energy changes in the reactions $A + B \rightarrow AB$, the following equation is used:

$$\Delta G_{AB} = [G_{AB}] - [G_A] - [G_B]$$  \hspace{1cm} \text{equation 8}

According to the reaction:

$$C_6H_2ClN_3O_6 + CN_3H_3 \rightarrow C_7H_4N_8O_6 + HCl$$  \hspace{1cm} \text{equation 9}

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

$$\Delta G_f = [G_{C7H4N8O6} + G_{HCl}] - [G_{C6H2ClN3O6} + G_{CN3H3}]$$  \hspace{1cm} \text{equation 10}

![Graph](image)

**Fig. 4** shows a diagram of the formation of $\Delta G_f$ for the synthesis of material 5-Amino-1, 2, 3, 4-tetrazole (PAT) from the reaction of substance 5-amino-1, 2, 3, 4-tetrazole with chloride picril at various temperatures.
The values of $\Delta G_f$ indicate that the synthesis process of Article 5 -pacril amino-1,2,3,4-tetrazole (PAT) from the reaction of substance 5 - amino-1,2,3,4-tetrazole with chloride picrilide at different temperatures is self-same and by increasing the process temperature, the Gibbs free energy changes become more positive, so the reaction is better at lower temperatures (Fig. 4).

**Discussion and conclusion**

The results of the calculations show that in the process of synthesis of Article 5, the amino-1, 2, 3, 4-tetrazol (PAT) of the reaction of the 5-amino-1, 2, 3, 4-tetrazole with chloride picril at various temperatures, the enthalpy is negative, which indicates that the process is calorific. As the reaction temperature increases, the heat released will be increased and the amount of an entropy $\Delta S_f$ is negative, which indicates that the irregularity has decreased in this process and with increasing temperature, the entropy becomes worse. The values of changes in the specific heat capacity in Article 5, Amino-1,2,3,4-tetrazole (PAT) and the primary substance 5-amino-1,2,3,4-tetrazole at various temperatures indicate that the product of the heat capacity Special is less. Under the same conditions, with less heat being taken up, the temperature of the feedstock increases, which indicates the high energy content of the original product relative to the primary material.

**References**


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