# Microreactor Based Flow Synthesis of 3-Nitro-1,2,4-triazol-5-one: A Novel Approach for Low-Sensitivity High Explosive

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**Abstract:** NTO (3-nitro-1,2,4-triazol-5-one) is classified as a common type of insensitive explosive, presenting a unique solution by combining low sensitivity to mechanical stimuli, such as impact and friction, with high thermal stability, all while manifesting performance characteristics close to RDX. Extensive literature has been published on NTO synthesis from its discovery in 1905 to the present employing traditional methods. This article experimentally presents novel approach, efficient and safe synthesis of NTO using microreactor flow technology. The results showed that Dimethylformamide (DMF) solvent and Dimethylformamide-Dimethyl sulfoxide (DMF-DMSO) combination serve as effective solvents for the nitration process within the microreactor. Only (5-minute) as a residence time was utilized significantly reducing reaction time of nitration process compared to the (1.5–2) hours required in traditional methods at 65 °C. This approach resulted in high yield of NTO production at a 1 M concentration achieving yields comparable to or slightly lower than those obtained through traditional techniques. The obtained intermediate and final products underwent analysis assessments by FTIR and DSC.

**Keywords:** 3-Nitro-1,2,4-triazole-5-one, Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO).

## 1. Introduction

The development of high explosive manufacturing has become a major focus for many scientists and researchers nowadays due to the serious problems and hazardous incidents associated with their production. These dangers and risks are not solely due to the use of hazardous reagents. But also, the various hazardous synthesis processes including nitration reactions, azide reactions and amination reactions, etc. also contribute significantly to the overall risk. Furthermore, other stages of handling, storage and transportation are also very risky and complicated [1-2].

1,2,4-triazol-5-one (NTO) is a heterocyclic compound having four nitrogen atoms. NTO exhibits high detonation performance with lower sensitivity to friction and impact compared to RDX, HMX and PETN while its sensitivity is close to TNT and TATB making it a promising insensitive explosive alternative to RDX in energetic materials compositions [3]. NTO already emerged as a potential solution for many explosive compositions such as B2267A and B2268A [4] that made by Nexter Munitions and IMX-101, IMX-104 [5] that developed to replace TNT in filling 155 mm M795 and 105 mm M1 projectiles and to substitute for Comp B explosive materials respectively. Furthermore, NTO and its derivatives are applied to in gun and rocket propellants [6] with different techniques used for the thermal stability studies [7].

A huge literature speaks about the synthesis of NTO. The first attempt to synthesis NTO was published by Manchot and Noll in 1905 [8]. Chipen et al. synthesized NTO reporting yield 67.5% of NTO [9]. Furthermore, Lee and Cobura [10] was succeeded in synthesis of NTO directly without separating the intermediate TO material in 1985. Spears et al. [11] have tried to optimize several parameters which affect the yield of NTO production. Becuwe and Delclos [12] improved the yielding of NTO up to 80%. While Smith and Cliff [13] synthesized NTO reporting yield 77% NTO.

Flow Chemistry refers to the practice of conducting the chemical reactions in a continuous flow system (microreactors) rather than the traditional batch chemistry. This technique uses channels or tubing to facilitate reactions in a continuous stream as opposed to using traditional flasks [14]. Microreactor systems are composed of various components including pumps, flow meters, reactors with controlled heating-cooling, separators, valves and analysis tools. Microsystems have a wide of applications including pharmaceuticals, polymers, nanomaterials, semiconductor and peptides [15]. One of the key advantages of this technology which attracts many researchers in its use in explosives synthesis, is its ability to ensure safety during the chemical transformations even at elevated temperatures and in the presence of hazardous reagents and products. These reactors facilitate rapid heating and cooling leading to precise temperature control and by minimizing the amounts of reagents that mixed together inside the microreactor [16]. Another advantage that makes microreactors a superior technology for synthesizing high explosives is their ability to mitigate hot spot formation during the production. Microreactors enable precise temperature control due to their small-scale dimensions allowing for rapid and accurate heating and cooling adjustments. Additionally, their high surface to volume ratio plays a crucial role in explosive material synthesis that enhancing the reaction efficiency and safety for these reasons [17].

(1) Enhanced Heat Transfer: The large surface area of microreactors promotes efficient heat transfer, crucial for dissipating heat in exothermic reactions and preventing excessive temperature increases within the reactor.

(2) Efficient Mixing: Microreactors guarantee uniform distribution of reactants through fast and efficient mixing, facilitated by their small dimensions. It enables rapid mixing in very short time that reduced the time of product in the reaction mixture.

(3) Increased Mass Transfer Rates: The microscale dimensions of microreactors facilitate efficient mass transfer of reactants and products. The increased mass and heat transfer rates contribute to higher reaction yields and selectivity.

Zuckerman et al. [18] successfully conducted safe nitration of 2,6-diaminopyrazine-1-oxide (DAPO) in a microreactor to produce high Explosive LLM-105.They emphasized the benefits of microreactor technology such as enhanced safety, precise temperature regulation, shorter reaction times. However, they reported that the process did not improve yield compared to batch synthesis maintaining a typical yield range of 50–60%. Karaghiosoff et al. [19] successfully synthesized nitroguanidine (NQ) in a microflow reactor in laboratory scale and industrial-scale production achieving a yield of 95% and a production rate of 58 g/h. Yu et al. [20] conducted the synthesis of high explosives TATB through a multi-step process. Their results demonstrated efficient nitration and a high yield of the final TATB product.

This work presents a novel approach for the synthesis of NTO as an explosive material. This approach addressing the challenges associated with the conventional synthesis methods of NTO. Notably, the conventional methods involve significant risks during the nitration step due to the relatively high nitration temperature of 65 °C for approximately 1.5-2 hours [11]. Moreover, the exothermic nature of the reaction throughout the nitration period poses additional challenges. During this duration, the temperature rapidly increases and can exceeds 100 °C within a few minutes, requiring the use of strong cooling system to reduce the temperature to 55-65 °C. However, the cooling system may cause the temperature to drop below 55 °C, requiring careful management to maintain the nitration temperature within the specified range. To address this issue, the process involves reheating to bring the temperature back within the desired range of 55-60 °C. This cycling effect may occur multiple times during the total reaction period, emphasizing the need for novel approach, efficient and safe synthesis of NTO using microreactor flow technology.

## 2. Experimental Section

### *2.1. Materials and Methods*

All chemicals, semicarbazied hydrochloride ($N_3H_5CO.HCL$), Formic acid ($CH_2O_2$ 88%) used in the preparation of TO and Nitric acid ($HNO_3$ 70%) were purchased from Sigma Aldrich. Additionally, all solvents, Dimethyl sulfoxide (DMSO), Dimethyl formamide (DMF), Acetonitrile, Chloroform, Ethyl acetate, Dioxan solvents were purchased from Sigma Aldrich and commercial sources. The starting material triazolone (TO) was prepared. Infrared (IR) spectra were recorded within the IR range of 400 – 4000 $cm^{-1}$ using Perkin Elmer SP-65, a device available at Polytechnique Montréal. Also, it is important to conduct the differential scanning calorimetric (DSC) experipments on the collected product through the SDT Q600 DSC model under $N_2$ flow, the heating rate was 1 °C/min and the sample mass approximately 0.5 mg. to confirm the thermal properties and to ensure the purity of NTO.

### *2.2 Preparation of TO*

TO was synthesized in a 500 mL three-necked flat-bottom flask equipped with a magnetic stirrer, thermometer and reflux system. The preparation involved adding 88% formic acid to solid semicarbazide hydrochloride at ambient temperature [11-12]. The reaction scheme is presented in figure 1. The mole ratio between the reactants is 1: 3 (SC.HCL: formic acid) respectively. Then the resulting solution was heated to 85-90 ° C and stirred magnetically for (6-8) hours at the reflux system. After the reaction completed, the excess formic acid was removed by evaporation until the triazolone precipitated. TO was washed with water and then evaporated once again to ensure removal of formic acid. Subsequently, the dried product was dissolved in heated water and slowly cooled until the product's precipitation, finally followed by filtration and drying at 60 ° C for 24 h.

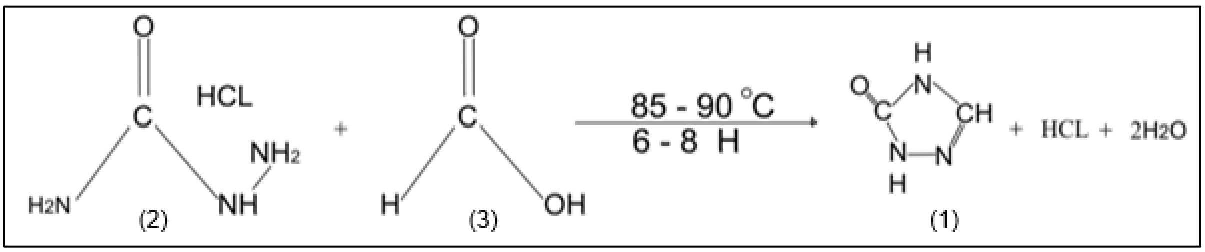


**Figure 1.** Batch synthesis of (1): 1,2,4 - triazole-5-one (TO). (2): Semicarbazide hydrochloride, (3): Formic acid.

### *2.3 Preparation of NTO*

Two Waters 515 HPLC pumps were utilized for the experiments. The flow rate of the pumps was adjusted to achieve the required mole ratio between the reactants and residence time in the reactor. Feed A and Feed B were combined and directed through the microreactor as shown in figure 3 which was maintained at the reaction temperature using Huber heater module. To ensure a stable and uniform flow, the system was purged before initiating the reactions effectively eliminating any air bubbles. Throughout the experiment strict safety precautions were implemented to minimize risks. Feed-A: Triazolone (TO) solutions of varying concentrations (0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1 M) were prepared in dimethylformamide (DMF) and other solvents as shown in table 1.

Feed-B: A 70% nitric acid ($HNO_3$) was used, following the optimized conditions in table 1, ensuring a consistent molar ratio of TO: $HNO_3$ at 1:5. The flow rates of both TO solutions and the stoichiometric excess of $HNO_3$ were maintained at constant values along with the reaction temperature resulting in uniform residence times within the microreactor.

At the microreactor outlet, the reaction mixture was directly collected in a product vial submerged in ice water for quenching. A 45 mL reaction mass sample was collected in each run for yield determination. The sample was then stored in a refrigerator for 24 hours to promote precipitation. The resulting NTO product was observed as a solid precipitate at the bottom of the vials. It was then filtered, washed with cold water and dried in an oven at 60°C for 12 hours. The yield was calculated based on the amount of TO fed into the system and the volume of reaction mass collected. After drying and weighing, NTO product was characterized using IR and DSC analysis spectroscopy. To clean the pump used for acid delivery, multiple solvents and flushing cycles were utilized. The cleaning process involved sequentially flushing the pump with water followed by sodium bicarbonate solution then isopropanol. For the other pump, acetone and isopropanol were used for thorough cleaning. The reaction scheme is presented in figure 2.


**Figure 2.** Synthesis of 5-niro-1,2,4 - triazole-5-one (NTO)

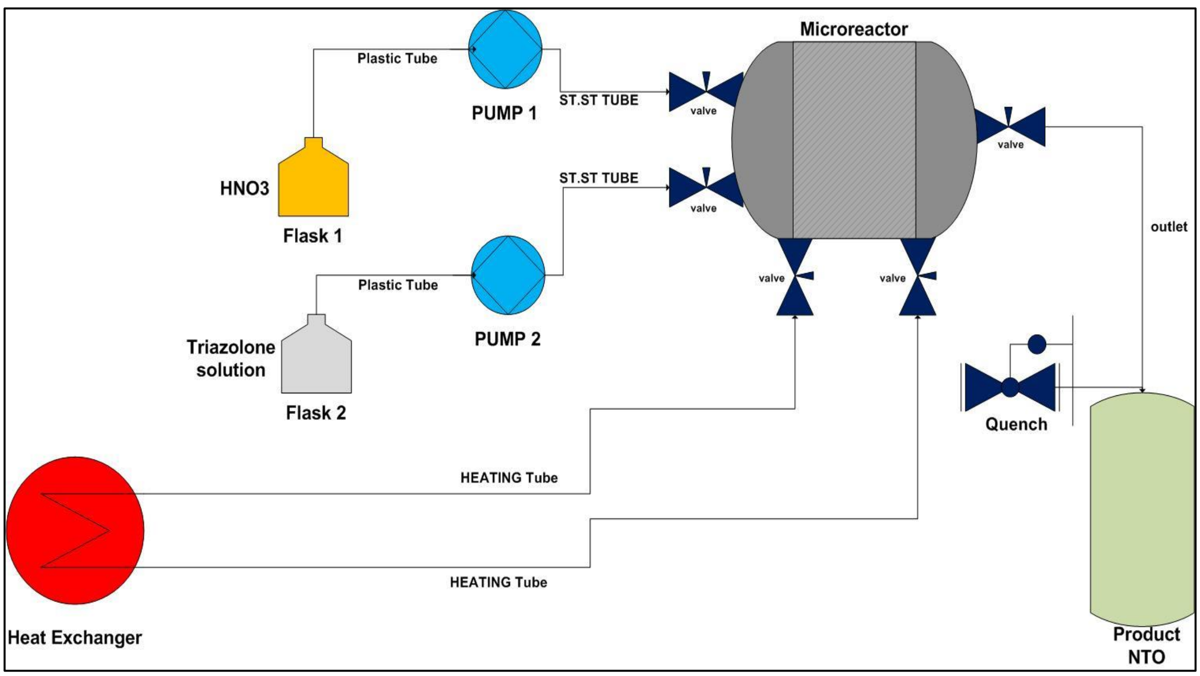


**Figure 3**. Schematic representation flow synthesis setup of NTO.

**Table 1**. Summary of Microreactor experiments for NTO preparation through flow chemistry.

| Run | Solvent | TO Concentration | $HNO_3$ [equiv] | Nitration temperature [°C] | Residence time [min.] | Yield % |
|---|---|---|---|---|---|---|
| R1 | DMF | 0.2 M | 5 | 65 | 5 | - |
| R2 | DMF | 0.4 M | 5 | 65 | 5 | - |
| R3 | DMF | 0.6 M | 5 | 65 | 5 | 31.89 |
| R4 | DMF | 0.8 M | 5 | 65 | 5 | 51.06 |
| R5 | DMF | 1 M | 5 | 65 | 5 | 57.41 |
| R6 | Acetonitrile: $H_2O$ (70:30) | 0.56 M | 5 | 65 | 5 | 29.90 |
| R7 | DMSO: $H_2O$ (90:10) | 0.8 M | 5 | 65 | 5 | 50.12 |
| R8 | DMSO: $H_2O$ (90:10) | 1M | 5 | 65 | 5 | 53.42 |
| R9 | DMSO: $H_2O$ (80:20) | 1M | 5 | 65 | 5 | 49.82 |
| R10 | DMSO: DMF (80:20) | 0.8 M | 5 | 65 | 5 | 52.31 |
| R11 | DMSO: DMF (80:20) | 1 M | 5 | 65 | 5 | 59.39 |
| R12 | DMSO: DMF (70:30) | 1 M | 5 | 65 | 5 | 56.25 |
| R13 | DMSO: DMF (50:50) | 1 M | 5 | 65 | 5 | 50.36 |

## 3. Results and discussion

*3.1 Synthesis of 1,2,4 triazole -5-one (TO)*

Triazolone was prepared by reacting solid semicabazide hydrochloride with formic acid as described in section 2.2. The yield of TO product is 71.45%.

*3.2 Solubility of TO*

The solubility of TO compound was investigated in various solvents. In DMF and DMSO, TO compound exhibited notable solubility allowing for the preparation of high concentration solutions of TO in theses solvents. The maximum solubility of TO in DMF was found to be approximately 1 M, whereas in DMSO, it reached approximately 2.8 M under standard atmospheric pressure and room temperature conditions. Conversely, TO compound demonstrated limited solubility in acetonitrile and it was insoluble in 1,4-Dioxane, Chloroform and Ethyl acetate under standard atmospheric pressure and room temperature conditions.

*3.3 Synthesis of NTO*

NTO was successfully prepared by reacting triazolone solutions with 70% $HNO_3$ as described in section 2.3 in a stainless-steel reactor trough flow chemistry. We assessed various solvents and TO reagent concentrations to determine their compatibility for use within microreactors. The results presented in Table 1 indicate that DMF, DMF: DMSO (80:20) and DMF: DMSO (70:30) are the most effective mixtures in terms of both solubility and reactivity yielding NTO at approximately 57.41%, 59.39% and 56.25% respectively. These results may be explained as presence of DMSO enhances the electrophilicity of $NO_2$+ ions then it may be increasing the nitration efficiency. On the other hand, experimental results indicate that when TO is dissolved in water containing solutions, the yield of NTO is consistently low compared with the above results approximately 53.42%. This can be attributed to the presence of water in the reaction medium which affects the nitration process by reducing nitronium ion $NO_2$+ electrophile formation. Then, the presence of excess water may shift the reaction equilibrium of the reaction backward and subsequently reducing nitration efficiency. Additionally at low concentrations, the yield is significantly reduced due to the fact that crystallization occurs when the reaction medium reaches supersaturation. At these lower concentrations, the amounts of NTO formed is minimal, preventing the solution from becoming supersaturated and as a result NTO remains dissolved in the reaction medium rather than precipitating. To confirm the formation of NTO explosives, the product of the experipments was submitted to FTIR analysis. Based on the spectra from figure 3, The characteristically bonds of NTO compound were identified confirming the nitration reactions. Also, the thermal properties of NTO were confirmed as shown in figure 4. It has a single exothermic peak 265.3 °C that confirm the decomposing of the NTO product. Also, there are no additional peaks that confirm the purity of the product.

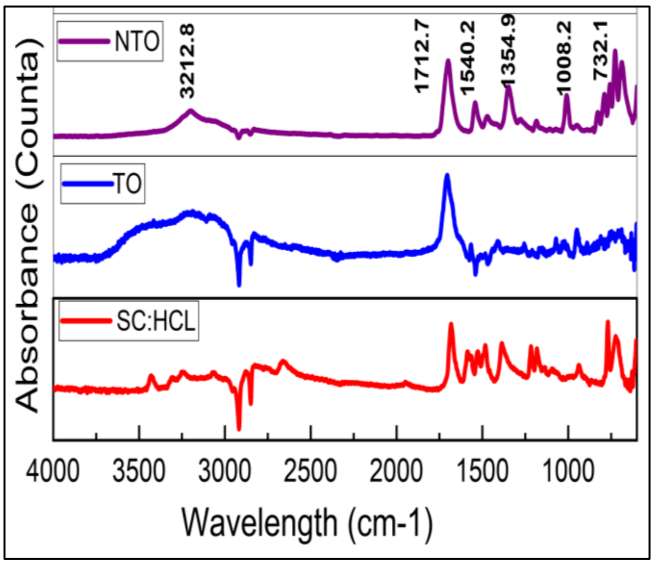


**Figure 4:** IR spectrum of semicarbazide HCL

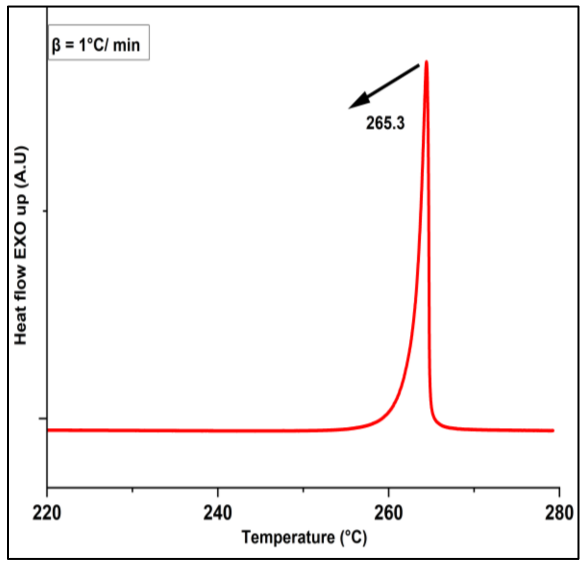


**Figure 5**: DSC curve of NTO (SC: HCL), triazolone (TO) and NTO.

## 4. Conclusion

NTO was successfully synthesized through the safe nitration of TO in concentrated nitric acid, utilizing a microreactor-based approach. Experimental results demonstrated that DMF and a DMF-DMSO combination serve as effective solvents yielding high NTO production when using a 1 M concentration, at 65°C, with a 5-minute residence time. This study represents a significant advancement in the synthesis of NTO explosives using microreactors and flow chemistry. However, it serves as an initial step as further optimization is required. Future studies should focus on key parameters such as temperature, residence time and reagent molar ratios to fully exploit the enhanced heat and mass transfer capabilities of microreactor technology.

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