

Synthesis and Characterization of Pentaerythritol Tetranitrate (PETN)

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Abstract

Pentaerythritol tetranitrate is considered a high explosive that has been widely studied for its chemical and mechanical properties due to its nitrate ester group structure. Its applicability is intended from military purposes to medicine and pharmacy. It is often a substitute for nitroglycerin and can be incorporated into polymeric matrices that enhance its properties and make it safer to handle. In this work a synthesis of direct form elaborated according to the reference material was presented, by the discontinuous nitration process, conducted in several steps starting from Pentaerythritol (PE) with fuming nitric acid, having a very significant and expected yield according to data referenced in previous studies. Fourier Transform Infrared Spectroscopy (FTIR-ATR), Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analyzes confirm the chemical structure of the substance obtained and the mass variation as a function of temperature, and typical information which can be derived from measurements such as characteristic temperatures (melting, crystallization, reactions, glass transition) for characterization of high energy materials. The explosive obtained by the new route proves to be effective and high yield.

Keywords: PETN; Nitrate Ester; FTIR; TGA; DSC; Energy Materials.

Introduction

Explosives are highly energetic materials that, when subjected to an external force, release large amounts of energy and gases at high temperatures, which result in a shock wave from the rapid expansion of these gases [1]. Polymer Bonded Explosives (PBX), form energy crystals aggregated into a polymer matrix. This class of energetic material has received great attention in scientific research for providing a high performance explosive, detonation sensitivity with high mechanical resistance that allow safe handling and logistics of the explosive [2]. Pentaerythritol tetranitrate, known as PETN, is one of the most studied explosives today. It is a nitrate ester with high sensitivity to explosion and is commonly used for military, industrial and even medical purposes [1]. PETN is a compound of crystalline structure. It has high chemical resistance, being the most stable of nitrate esters, and low sensitivity to mechanical forces. The gaseous by-products released in the PETN explosion are directly related to the activation medium, which may lead to NO₂, NO, N₂O, N₂, CO₂, CO, H and O₂ [3]. It has a high detonation temperature, due to the large amount of oxygen, low vapor pressure and, consequently, low dispersion in the environment [4]. Thermal stability of PETN may be affected by factors such as particle size and crystal lattice instabilities [5], suggesting the reduction of crystal size to micro

scale, which allow corrections of instability problems. The has polymorphic variations: PETN-I, or α -PETN, tetragonal structure and PETN-II, also known as β -PETN, with orthorhombic formation. PETN-II can be converted to PETN-I, most commonly at 130°C [6].

As a high performance explosive, PETN is widely used for military purposes as a secondary detonator explosive. In the commercial field, nitrate esters are used as drug vasodilators. Its applicability expands by obtaining Semtex, a plastic explosive composed of PETN and a polymer matrix in different proportions that attributes mechanical properties, often used as demolition explosives in mining activities and even in environmental quality control testing [7]. There are two routes for PETN synthesis, both starting from pentaerythritol as a substrate. The mixed route employs a mixture of nitric and sulfuric acids known as sulfonidric mixture. This route was once very important in the explosives industry, but it generates many sulfonated byproducts that compromise the efficiency and chemical stability of the end product. The other route is by nitration with concentrated nitric acid (96-98%) at 50°C, which is of direct importance in the production of nitrate esters by providing better yields and dispensing complex purification processes. Both include in the esterification of alcohol with the corresponding acid, where the hydroxyl groups will become nitrate ester groups [8]. The present work aims to present the

synthesis of pentaerythritol tetranitrate with nitric acid, presenting its subsequent characterization and reaction yield.

Experimental Method

The synthesis route of PETN adopted in this work was via fuming nitric acid 99.5% PA (Química Moderna, Brazil), in a two-stage batch: nitration of pentaerythritol alcohol (Sigma Aldrich), followed by subsequent precipitation of pentaerythritol tetranitrate. Discontinuous nitration is widely used in small quantity processes using batch reactor. The whole process of nitration synthesis is prepared at low temperatures because the reaction is highly exothermic. An extra ice bath is prepared for emergency cooling if the temperature exceeds a 25°C safety limit. Infrared (IR) analyzes were recorded on a Perkin Elmer Spectrum One spectrophotometer in the region of the 4000 cm⁻¹ to 500 cm⁻¹ spectral range, number of scans 8 if the reaction triggered. In accordance with safety regulations, the temperature for unloading is a maximum of 30 °C. Spectrometric characterization was performed using a spectrometer in the region of 4 cm⁻¹ resolution. The samples were analyzed by infrared with the aid of the ATR (Total Attenuated Reflectance) accessory. The test method and procedures for obtaining the spectra of PETN specimens were by means of potassium bromide (KBr) pellets, which are generally applied to solid samples in powder form. The Thermogravimetric technique is used when one wants to track mass variations involved in an experiment with quantitative results. TG curves were obtained on a thermogravimetric analyzer (SDT Q600 V20.9 Build 20), with a heating ratio of 10°C min⁻¹ under a nitrogen atmosphere (N₂), with a mass of approximately 9 mg with platinum crucible. in the temperature range 28 - 800°C. In accordance with the standard established by ASTM D6370-99. To determine the temperature ranges corresponding to the percentages of hydration, decomposition of organic material and residue formed, TGA curves, corresponding to the first derivative of TG curves, are used. The TG curves of the samples were obtained to verify the thermal decomposition profile.

Nitration of Pentaeritritol

The alcohol used was monopentaerythritol (PE) sold by Sigma Aldrich, Germany; and nitric acid (HNO₃) 99.5%, sold by Química Moderna. Initially an ice bath (water, ice and NaCl) was prepared. 99.5% HNO₃ was added to a 200 mL beaker and allowed to cool in the bath while maintaining the temperature range of 15°C to 20°C. The PE was placed in five 2g quotas, totaling 10g. Each portion of the anhydrous alcohol was added to the 99.5% HNO₃ solution (5: 1 ratio of acid and alcohol, respectively) at short intervals under constant manual stirring and temperature control. Excess acid is required to ensure complete dissolution of the explosive and complete PE nitration. Otherwise, pentaerythritol dinitrate and trinitrate compounds appear, causing the melting point to be reduced. During the synthesis, an intense exothermic reaction is observed characterized by the temperature increase and also the solution thickening. The temperature range between 15°C to 20°C is the key to synthesis. If leaking nitration occurs, as evidenced by the evolution of brown N₂O₄ / NO₂ gas, the mixture should be immediately discharged into the emergency bath to stop the reaction for safety reasons. In about 10 minutes the solution becomes thick and white in color. After addition of the last 2 g of PE, stirring is continued for a further 10 minutes.

Pentaeritritol Tetranitrate (Petn) Precipitation

The precipitation step follows de-acidification processes with

sodium carbonate (Na₂CO₃), sold by P.A Synth, Brazil, and with acetone, sold by Química Moderna, Brazil. The mixture is diluted in 450 ml of cold deionized water for precipitation of the explosive, maintaining the temperature range between 15°C and 20°C. Excess deionized water is decanted after crystalline deposition to facilitate product filtration. This step is crucial in determining the size and quality of the crystals. Lower temperatures and a lot of agitation can lead to very fine crystals, impairing the filtration of the material. Therefore, agitation conditions and temperature are determining factors, being carefully controlled. The contents are passed through a filter screen, which is washed with ice-cold deionized water and then preliminarily neutralized with 10% Na₂CO₃ hot solution. With this operation, the acidity adhering to the crystals is eliminated, leaving the occluded acidity. The material undergoes careful filtration with vacuum pump until it becomes a thickened compound. The wet compound is transferred to 200 mL of 10% acetone solution at 50°C. The solution is kept under stirring and temperature control until complete dissolution. Excess acetone solution is required due to excess water present from the densified material to ensure total. Some works found in the literature suggest drying the material before the recrystallization process. The PETN / Acetone solution is added to 600 mL of ice-cold deionized water, causing the PETN crystals to be deposited to the bottom of the beaker. The conditions of temperature, agitation and water addition rate are determinant in the granulometry of the crystals. Final compound is filtered through a screen filter under constant washing with deionized water to completely eliminate acetone solution. The final product is finally deposited in oven drying petri dishes with air circulation at 60°C. The explosive is finished at a rate of 0.5% moisture content as required by the literature[9].

Results and Discussion

Theoretical Income

The nitration reaction of PETN through the direct action of concentrated nitric acid on pentaerythritol, according to [10] and other studies found in the literature, yields approximately 95% through the following reaction: $\text{CH}_3\text{CHO} + 4 \text{CH}_2\text{O} + 4 \text{HNO}_3 \rightarrow \text{C}(\text{CH}_2\text{ONO}_2)_4 + 4 \text{H}_2\text{O}$



By stoichiometry, 100 kg of PE will produce 232.5 kg of PETN:
 $316/136 \times 100 = 232.5 \text{ kg}$

Practical Income

10 g of Pentaerythritol results; 22.5 g PETN (crude) - Yield $(22.55 / 23.25) \times 100 = 96.8\%$; 22.25 g PETN (purified) - Yield $(22.25 / 23.25) \times 100 = 95.6\%$

Infrared Spectroscopy With Fourier Transform And Thermogravimetric Analysis.

Characterization analyzes such as Fourier Transform Infrared Spectroscopy and Thermogravimetric Analysis are of paramount importance for the information provided, such as precise frequencies of vibrational spectra, chemical, structural composition, decomposition temperatures and gradual mass loss until their final decomposition and presence of PETN functional groups for studies available in the literature [11,12]. (Figure 1).

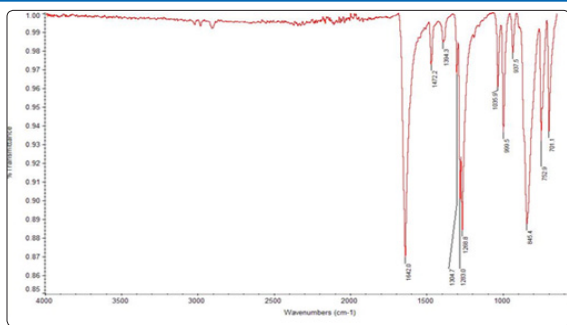


Figure 1: PETN FTIR Spectrum (4000-500 cm^{-1}).

The symmetric and asymmetric elongation vibrations of the nitro group (NO_2) give rise to two distinct absorption bands. These $-\text{NO}_2$ stretch vibrations in nitrate esters appear at 1285-1270 cm^{-1} and 1660-1640 cm^{-1} , which are characteristic of the functional group that can be seen on PETN infrared. The transition that occurs between these two energy levels is by the absorption of radiofrequency (IR) radiation, called resonance. The observed peaks were consistent across the infrared spectrum, with some slight variations in peak rates. Peak positions were found when compared to previous studies according to the literature [13,14,15].

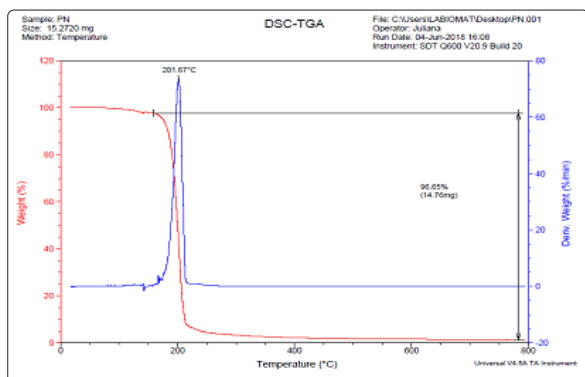


Figure 2: The PETN thermogram, TGA-DSC trace for the energy material heated to $50^\circ\text{C min}^{-1}$.

Thermogravimetric analysis was used to verify the thermal decomposition of the PETN, the samples (approximately 15.5 mg) were loaded in an open platinum crucible, the analytical movement focused on an initial isothermal retention at operating temperature of 28°C to 30°C . The thermogram showed a very gradual mass loss between 28 165°C and 165°C , losing around 1% of the total mass. Above 165°C , the loss is faster but still constant for PETN. The rate of mass loss remained constant between 165 201°C of lost PETN (96.65%), close to 14.76 mg of total mass. The thermal curve profile of PETN presents the decomposition of the high energy material, the DSC shows an expected behavior for the sample according to the experimental physical properties. The DSC curve of PETN indicates a single endothermic fusion temperature and another exothermic decomposition temperature were observed. Based on the fact that PETN decomposes from the liquid state, since fusion occurs around 143°C . The maximum exothermic temperature is around T_{max} . at $10^\circ\text{C / min} = 212^\circ\text{C}$. And exothermic mass loss temperature is around T_{max} . at $10^\circ\text{C / min} = 202^\circ\text{C}$. The values related to the thermal decomposition process are close to the literature according to the material analysis (PETN), revealed by the exothermic mass loss curve profile.

Conclusion

The explosive synthesized by the new route proved to be effective,

with yields above that mentioned in the literature, which claims around 95%, obtaining amounts of 96.8% (gross) and 95.6% (purified). The FTIR shows the same characteristics as PETN according to the literature. TGA-DSC (PETN) analyzes revealed the profile of the exothermic mass loss curve according to the literature. Overall, the elaborated synthesis proved to be a success. Following this work, the refining of the synthesis will be performed in order to obtain purified PETN in larger quantities for use as active ingredient of pharmacological applications.

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