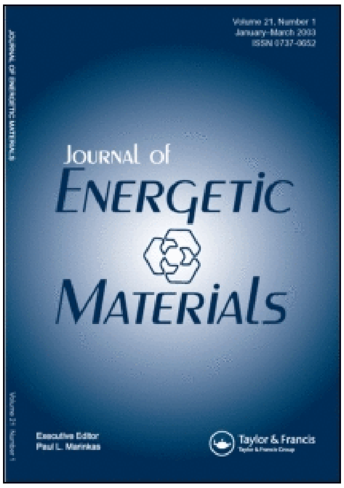

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Process Optimization for Synthesis of CL-20

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Process Optimization for Synthesis of CL-20

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Optimization of process parameters for synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) of desired particle size have been described. CL-20, the most powerful high explosive, is being synthesized at the High Energy Materials Research Laboratory (HEMRL, Pune, India) by nitration of 2,6,8,12-tetra-acetyl-2,4,6,8,10,12-hexaazaisowurtzitane (TAIW). Nitration of TAIW is a mild exothermic reaction. Although information on synthesis of CL-20 is reported, no information is available on process optimization. In order to optimize the process parameters for synthesis of CL-20 to obtain higher yield and purity, a study was carried out with variation of different parametric conditions like temperature, time, concentration of nitric acid, mole ratio of reactants, quantity of solvent/anti-solvent, etc. The effect of each parameter was studied by keeping other parameters constant. In the present study it was found that for ∼85% yield, optimized temperature envelope was 72–85°C, nitric acid concentration range from 98 to 92%, reaction time was 1 h, and temperature during the addition of TAIW into the mixed acid was 25–40°C. In order to improve the particle size of CL-20, during the recrystallization process, the effect of parameters like addition rate of anti-solvent and rate of agitation were studied and

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optimum conditions identified. CL-20 synthesized under optimized conditions was characterized and confirmed by different analytical methods like ^{1}H-NMR, Fourier transform infrared spectroscopy (FTIR), elemental analysis, differential scanning calorimetry (DSC), etc. Purity of CL-20 was estimated by high-performance liquid chromatography (HPLC). Particle size of ~150 µm *was achieved by crystallization under optimized process conditions.*

Keywords: CL-20, crystallization, nitration, TAIW

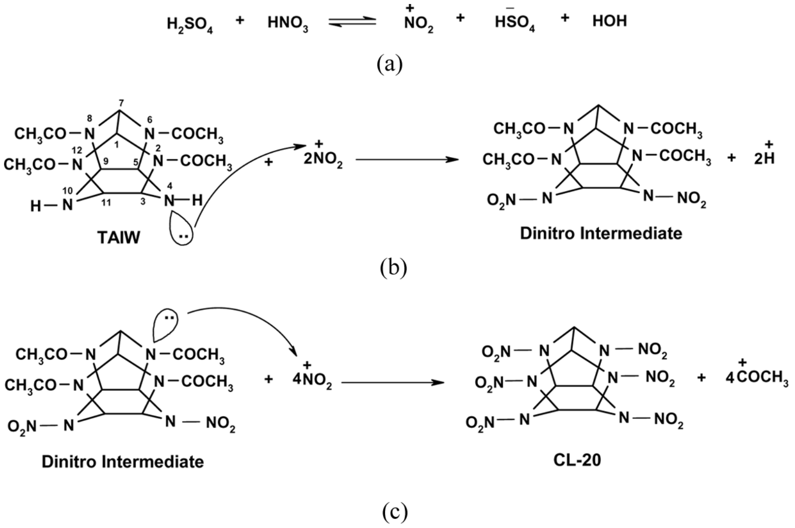
Introduction

CL-20, first synthesized by Nielsen [1], is the most energetic and futuristic high explosive. It is a potential candidate to replace HMX [2]. Balas et al. [9] of the U.S. Army TACOM-ARDEC. Thiokol Propulsion have evaluated various formulations based on CL-20, HMX, and RDX. The study revealed that CL-20-based formulations yield a 42% increase in total energy and a 28% increase in expansion energy over HMX/RDX-based formulations. Due to the high energy content of these cage-like molecules, the detonation pressure is very high, more than double that of TNT [3]. The development of CL-20 is accelerated for applications where performance is of importance. Due to its excellent performance, it has gained significant interest in the recent past. It is good for tactical applications both in propellants as well as in explosive composition. Synthesis efforts have been made for a number of nitrolysable precursors to CL-20 including isowurtzitane cage substituted with nitroso [4], formyl [5], and acetyl [6] groups. Synthesis of CL-20 from tetraacetylisowurtzitane (TAIW) has appeared as a favorable method, both in terms of process economy and product purity. The High Energy Materials Research Laboratory has established a process for the preparation of CL-20 by nitration of TAIW [7]. Because no literature is available regarding the process optimization, a study was undertaken to determine the same for the parameters like temperature, time, concentration of nitric acid, moles of nitric acid, and crystallization of CL-20 to get the desired particle size. During the study, only one parameter was varied, keeping all other parameters constant. Predetermined quantities of TAIW and mixed acid were allowed to react at a fixed temperature for different reaction periods to generate a concentration profile. The aim was to obtain a preliminary idea of the reaction time.

Experimental

Reaction

Nitration of TAIW was carried out at moderate temperature and the reaction was mild exothermic in nature. A mixture of concentrated sulfuric acid and nitric acid was used as nitrating agent. TAIW was added slowly into the mixed acid at room temperature in the mole ratio of TAIW : HNO_3 : H_2SO_4:: 1 : 64 : 12. The reaction mass was then heated to 85°C and maintained for 1 h. The mechanism of formation of nitronium ion and the progress of the reaction were expected to involve the steps shown in Scheme 1. In the presence of sulfuric acid, nitric

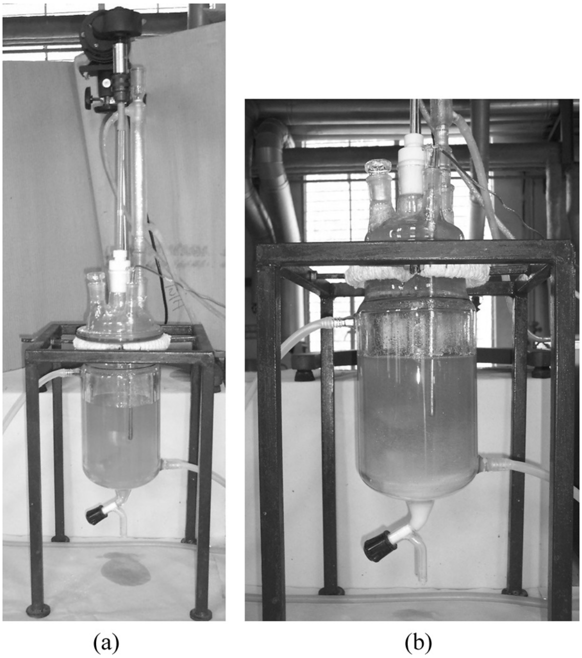


Scheme 1. Reaction mechanism.

acid underwent ionization to generate nitronium (NO_2^+) ions, and TAIW underwent electrophilic substitution reaction at nitrogen atoms by the electrophile NO_2^+ ion to give the nitrated product; i.e., CL-20.

Experimental Setup

The experimental setup (Figs. 1a and 1b) consisted of a cylindrical jacketed glass reactor (2 L) fitted with a driving motor, agitator, and temperature sensors/indicators inside the reaction as well as a jacket inlet/outlet and PID-controlled hot and cold water circulation unit (5-L capacity) for heating/cooling the reaction media to maintain the temperature. A water-cooled glass condenser was fitted on the top of the reactor and a flush-bottom Teflon valve was fitted at the bottom of



(a) (b)

Figure 1. (a) Reaction assembly and (b) reactor with precipitated product.

the reactor. The whole reaction assembly was skid-mounted on a metal stand for easy accessibility.

Experimental Procedure

Commercial tetraacetyl isowurtzitane (TAIW) [8], purity ~98%, was used as the starting raw material for the synthesis of CL-20.

Twelve hundred milliliters of HNO_3 was taken in the reactor and 300 mL H_2SO_4 was added slowly with stirring. To this acid mixture, 150 g of TAIW was added in 15 min; during the addition of TAIW, the temperature of the reaction mass increased from ambient to 45°C. It was assured that there was no lump formation in the reaction mixture during the addition of TAIW. The reaction mixture was then heated to 85°C, using hot water circulation. The product started forming as a white precipitate. RPM of agitator (110–120) was maintained for 1 h at 85°C and then allowed to cool to 20°C by circulating cold water through the jacket. The reaction mixture was poured over crushed ice (3 kg) slowly under controlled temperature with stirring. Crude CL-20 was filtered through polypropylene cloth filter and washed thoroughly with water.

The crude product was dissolved in 540 mL of ethyl acetate. The ethyl acetate solution was washed with 200 mL saturated aqueous $NaHCO_3$ followed by 300 mL saturated aqueous NaCl. The ethyl acetate layer was separated and dried by passing through an anhydrous Na_2SO_4 bed. The dried solution was taken in a round-bottom flask fitted with an agitator; heptane (1600 mL) was added under stirring (RPM 80–100) for a total time of 1 h. The precipitated product was filtered and dried at room temperature. A second crop was also collected from the filtrate, first by removing the solvent and then repeating the same crystallization process. Yield of CL-20 was 161.2 g (82.4%) having a median particle size of ~150 μm.

For recrystallization CL-20 was dissolved in ethyl acetate (0.5 g/mL). Arrangements were made for the mechanical stirring and controlled addition of the anti-solvent, heptane. When the solution became clear, heptane (three times of ethyl acetate volume) was added under different addition and agitation rates. When the addition was over, the precipitated material was collected by filtration followed by drying at room temperature (recovery was ~90%). Experiments were carried out at 5 g/batch level.

Results and Discussion

In order to optimize nitration parameters like reaction temperature, moles of nitric acid, concentration of nitric acid, temperature of addition of TAIW in mixed acid, agitation of the reaction mass, etc. Several set of experiments were conducted for each parameter, keeping other parameters constant. After completion of each experiment, the reaction mixture was quenched using crushed ice. Crude product was then isolated by filtration. This product was crystallized from ethyl acetate by adding heptane as anti-solvent. The product was filtered, dried at room temperature, and characterized.

Effect of Temperature on Addition of TAIW in Nitrating Mixture

It was reported [7] that addition of TAIW in mixed acid is necessarily to be carried out at 0–5°C, which essentially requires a cryostat unit to maintain such a low temperature. In order to optimize this parameter, experiments were conducted where TAIW was added at different temperatures of 5, 10, and 25°C, keeping other parameters constant. Product obtained from these batches was analyzed and it was observed that yield and purity were similar to that of batches reported at low-temperature (0–5°C) addition. Therefore, 25°C was selected under controlled addition, because it does not require any cooling or heating for TAIW addition.

Reaction Temperature Envelope

Nitration of TAIW is a mild exothermic reaction. During nitration, formation of hazardous side products like acetyl nitrate [6] cannot be ruled out, which may explode violently if heated excessively. Hence, it is essential to know the operating temperature envelope at which the reaction has a maximum yield and optimum heat generation. Previously, it was reported [7] that the temperature for nitration of TAIW is 76 ± 1°C. In order to generate the temperature envelope, nitration was conducted at 70, 76, 80, and 85°C, and the process was found safe in the temperature range of 80–85°C and yield was also greater. It was observed that beyond 85°C, formation of NOx gases increased significantly, which is not desirable. Thus, the approximate temperature envelope for the reaction is 83 ± 2°C. Below 80°C a reaction takes place but the reaction time is prolonged by an additional 2 h.

Effect of Reaction Time

Reaction time is very important for any chemical reaction, particularly when the reaction is done under elevated temperature and with excess moles of acids. Allowing the reaction to continue for an extended time may lead to the degradation of the product, resulting in wastage of the resources; on the other hand, insufficient reaction time results in an incomplete reaction. Therefore, efforts were made to optimize the reaction time. The reaction was studied from 2 min to 4 h (Fig. 2). It was observed that the maximum purity of the product was obtained for a period of 1 h reaction.

Previously, for the synthesis [7] of CL-20 at HEMRL, reaction time reported was 4 h at 76 ± 1°C without any agitation of the reaction mixture. This reaction was exothermic in nature and it is not recommended to be carried out without agitation, because it may accumulate heat and subsequently lead to a runaway reaction. So a reaction assembly was arranged to provide agitation to the reaction mixture. With agitation and a slight increase in the reaction temperature (increased to 83 ± 2°C), the reaction time was optimized to 1 h.

Effect of Nitric Acid

Moles of Nitric Acid. Nitration was studied by carrying out experiments with 24 to 64 mole equivalents of nitric acid

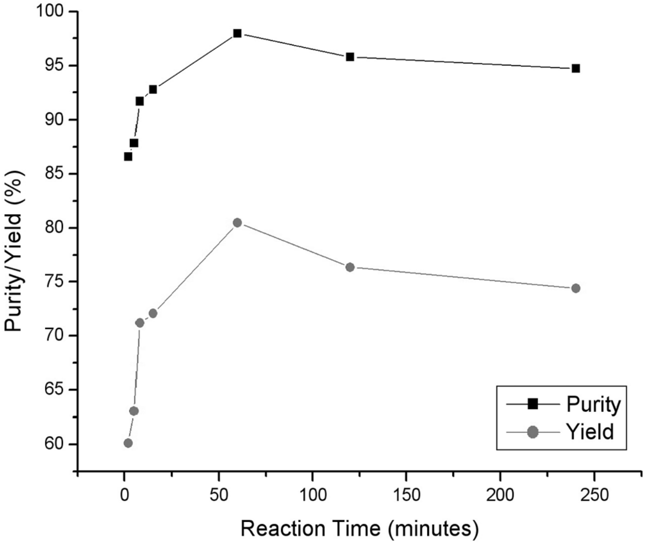


Figure 2. CL-20 purity and yield vs. reaction time.

(98%). It was reported that the reaction rate was more dependent on the solubility and the rate of solvation than the nitration rate [6]. Nitrogen atoms of TAIW at 4 and 10 positions are more reactive because the lone pair of electrons with these nitrogen atoms was more available for an electrophile attack, compared to other nitrogen atoms, which are attached to electron-withdrawing acetyl groups. As a result, the first substitution took place at 4 and 10 positions followed by other caged nitrogen atoms. To increase the reaction rate, it is important that more intermediates (partially nitrated products) should be in the dissolved form, which can be achieved by more dilute substrate concentration, but after a certain limit this is not economical. It was observed that to obtain a product of high purity and yield, 64 mole equivalents of HNO_3 were required, which was ~11-fold in excess of the theoretical requirement (Fig. 3), below which the yield came down drastically.

Strength of Nitric Acid. To study the effect of strength of nitric acid on the purity and the yield of the product, experiments

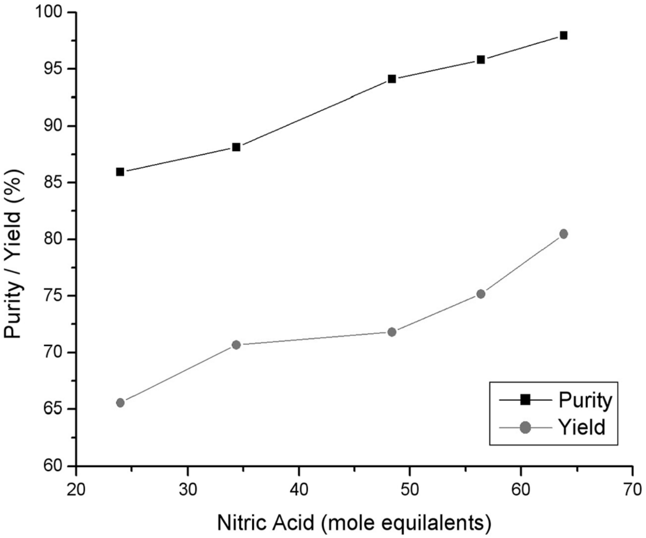


Figure 3. CL-20 purity and yield vs. nitric acid (mole equivalents).

were carried out with nitric acid having strength of 89–98%. As expected, the purity and the yield of the product came down as the strength of the nitric acid was brought down (Fig. 4). This is because the nitronium ion concentration and the solubility of partially nitrated products reduced as the water content increased in the nitric acid. Maximum yield and purity of CL-20 was obtained with 98% HNO_3.

Crystallization

Purification of the material with desired particle size distribution was achieved by a crystallization process. As in the field of energetic material formulations, the particle size of the energetic ingredients plays an important role in determining the performance of the formulation. Hence, effort was made to optimize the crystallization parameters to prepare the material in different particle size distributions.

For crystallization to occur, the solution must be supersaturated. This was achieved by various methods, including

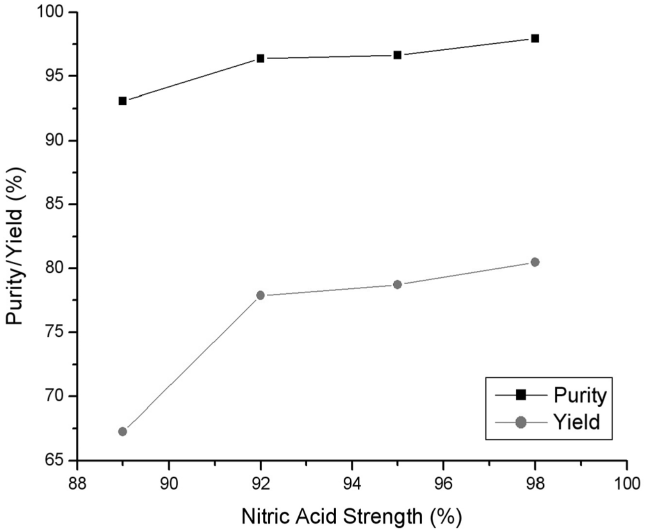


Figure 4. CL-20 purity and yield vs. nitric acid strength.

solution cooling, solvent evaporation, addition of a second solvent to reduce the solubility of the solute (known as anti-solvent or drowning crystallization), etc. In the present study, addition of a second solvent to reduce the solubility of the solute was used. Variation has been made in the addition rate of the second solvent and the agitation of the solution. Important factors such as vessel type, stirrer type, temperature, impurity level, etc., play a major role on the size and shape of the crystal. These factors were kept the same for all experiments. The crystallization process was optimized to produce particle sizes ranging from 10 to 200 µm.

The particle size measurement was done using a Malvern Mastersizer 2000 (HEMRL, Pune, India), in a water suspension (Table 1). The particle size and shape were also determined by scanning electron microscopy (Figs. 5a and 5b).

Particle size of about 10 µm was achieved by the reverse precipitation process where the saturated ethyl acetate solution of CL-20 was poured at a very fast rate into the haptane with efficient stirring.

Table 1
Data on crystallization study of CL-20

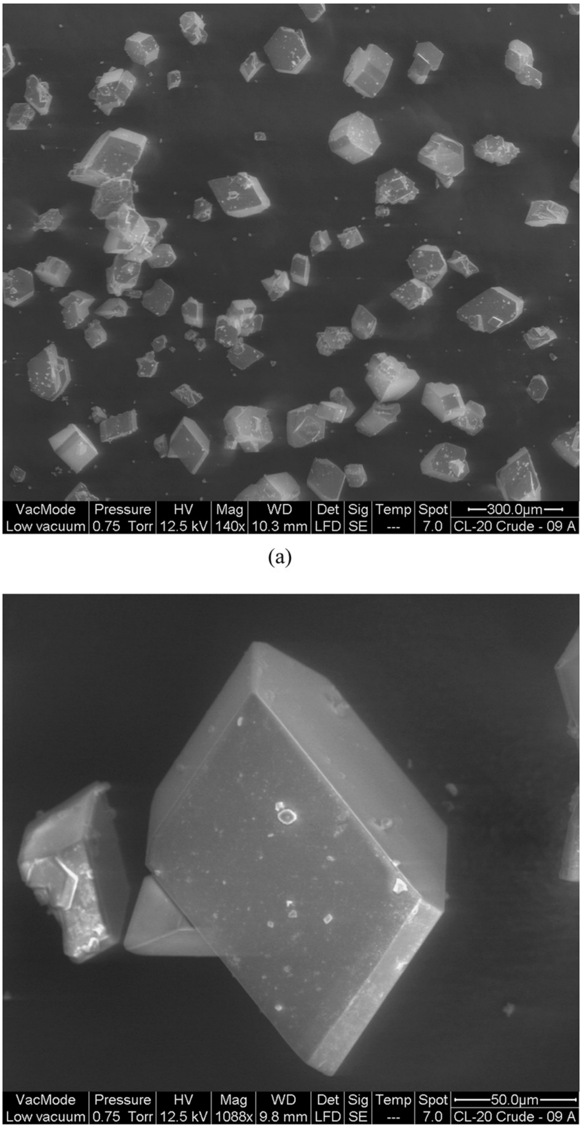
S.no.	Heptane addition rate (mL/min)	RPM	Particle size (µm) d (0.5)
1.	1.5	80–100	98
2.	1.5	20–40	106
3.	0.75	80–100	123
4.	0.75	20–40	194
5.	Fast addition	250–280	43

Product Characterization

CL-20 produced during the study was characterized by various analytical tools.

Spectroscopic and Elemental Analysis

Structural confirmation of the product obtained by the above-mentioned method was done by ^{1}H-NMR, Fourier transform infrared spectroscopy (FTIR), and elemental analysis. Structural features were satisfied by the spectroscopic data. The ^{1}H-NMR spectra (recorded on a Varian Mercury YH-300 MHz (Pune University, Pune, India) instrument using tetra methyl silane as an internal reference and acetone-d_6 as solvent) showed two singlets at 8.05 and 8.19 δ having a peak ratio of 1:2. The singlet at 8.05 δ corresponds to two protons at position 1 and 7, and the singlet at 8.19 δ corresponds to four protons at the positions 3, 5, 9, and 11 (Fig. 6). UV spectra obtained from a Hitachi U-3310 Spectrophotometer (HEMRL, Pune, India) using acetonitrile as solvent. The wavelength at which maximum absorbance of light took place ($\lambda_{\max}$) was 226 nm, which matches the reported value of $\lambda_{\max}$ for CL-20. FTIR (in KBr pellet) spectra showed the presence of cage C-H (3039 cm^{-1}) and NO_2 (1604, 1558, 1334, and 1274 cm^{-1}) bond stretching. Elemental analysis was carried out on a Perkin Elmer Elemental Analyzer EA-1110 (HEMRL, Pune, India). The elemental analysis results were found to be in close



(a)

(b)

Figure 5. (a) SEM image of CL-20 crystals and (b) SEM image of single CL-20 crystal.

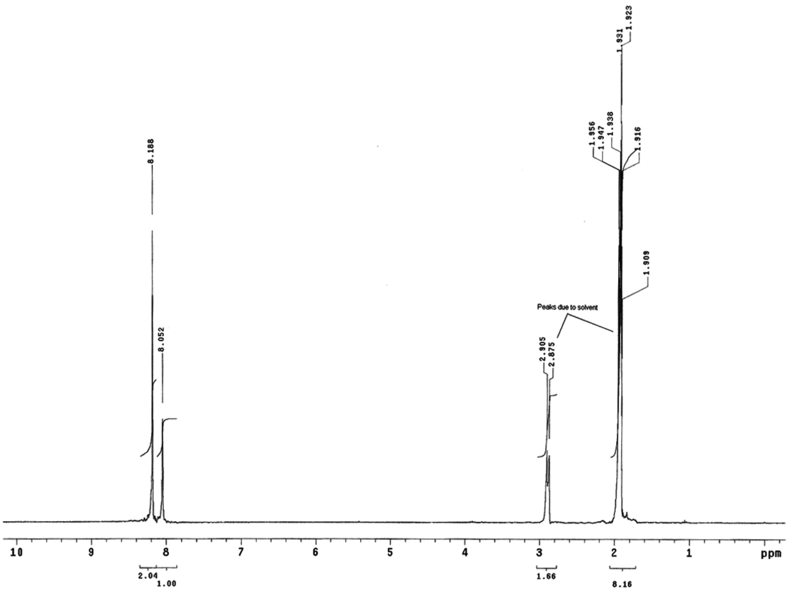


Figure 6. ^{1}H-NMR spectrum of CL-20.

agreement with the theoretical elemental composition (calculated for $C_6H_6N_{12}O_{12}$: C 16.45%, H 1.38, N 38.36). The product showed elemental composition of 17.14% carbon, 1.23% hydrogen, and 39.16% nitrogen.

Thermal Analysis

Thermal characterization of the product was done by differential scanning calorimetry (DSC; Perkin Elmer Model Pyris-7, HEMRL, Pune, India). Heating rate was 10°C/min under nitrogen atmosphere and the sample size was ~0.5 mg. The product exhibited a single exotherm with temperature maxima ($T_{\max}$) at 253°C (Fig. 7).

Chromatographic Analysis

High-performance liquid chromatography (HPLC) was used to confirm the purity of CL-20. A method for the HPLC analysis of the product was established. Eluent consisted of

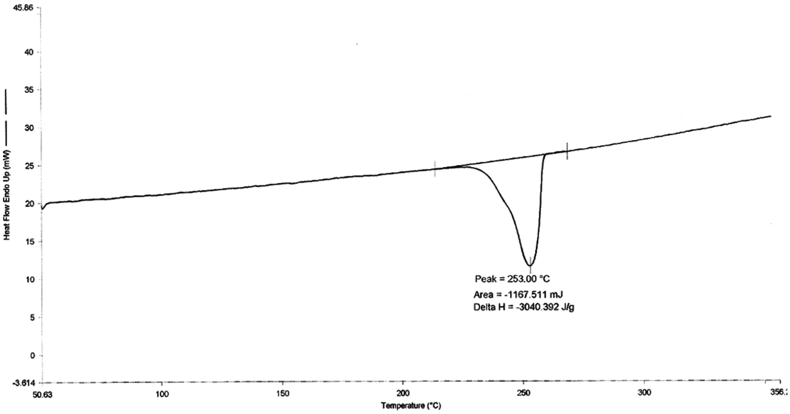


Figure 7. DSC thermogram of CL-20.

acetonitrile-water in the ratio 45:55 (isocratic), at a flow rate of 1 mL/min with the UV detector at 226 nm. The retention time of CL-20 was 8.9 min in the C-18 column (Fig. 8). Because the CL-20 in its pure form was not available commercially, for the quantitative analysis of the product, CL-20 was purified by repetitive crystallization followed by column chromatography. The CL-20 synthesized by the above-mentioned method was found to have a purity of ~98%.

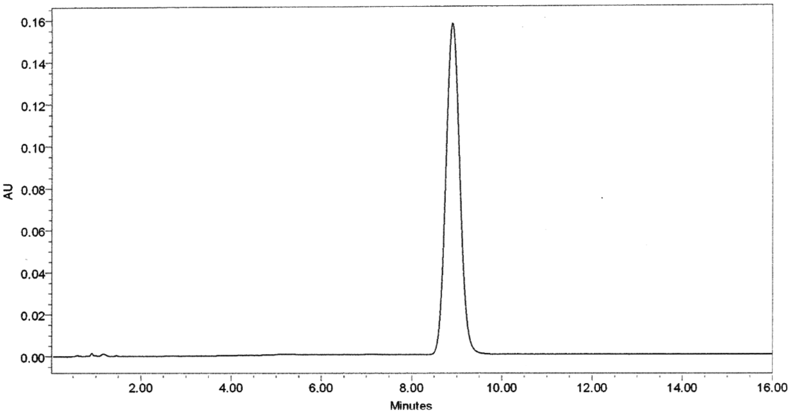


Figure 8. HPLC chromatogram of CL-20.

Sensitivity Analysis

The sensitivity to impact was determined by the fall hammer method using a 2-kg drop weight. The results are reported in terms of height for 50% of explosion ($h_{50\%}$) of the sample. The friction sensitivity of the compound was measured on a Julius Peter's apparatus. The results obtained for impact and friction sensitivity were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively. The impact and friction sensitivity of the product were found to be 31 cm and 10.4 kg, respectively, compared to 40 cm and 13 kg, respectively, for HMX.

Conclusion

Reaction parameters for the nitration of TAIW were optimized to obtain a better yield and high purity of CL-20. Using optimized reaction conditions, synthesis was carried out at 150 g/batch level of CL-20. The parameters optimized during this work are useful for developing technology for the production of CL-20 at higher scale. Efforts were made to ensure the quality of the product; it was analyzed by the ^{1}H NMR, elemental analysis, FTIR, UV, DSC, and HPLC.

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