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Higher performance and safer handling: new formulation based on 2,2,2-trinitroethyl formate and nitrocellulose

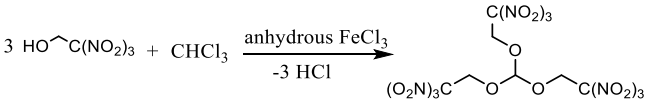
Mohamed Abd-Elghany[a], Thomas M. Klapötke*[a], Burkhard Krumm[a] Ahmed Elbeih[b]

Dedicated to Professor Dr. Wolfgang Bensch on the Occasion of his 65th Birthday

Abstract: The novel, green propellant formulation based on the new interesting high energy dense oxidizer (HEDO) 2,2,2-trinitroethyl formate (TNEF) and nitrocellulose (NC) was prepared and thermally investigated using nonisothermal thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TNEF has been successfully synthesized and characterized by nuclear magnetic resonance (NMR) and FTIR spectrometer. Scanning electron microscope (SEM) was used to check the crystals of the oxidizer and the homogeneity of the new propellant formulation (NC-TNEF). The burning behavior of NC-TNEF was recorded by high-speed camera to observe the smoke produced. A high specific impulse (I_s = 257.4 s) was obtained from the characteristics calculation of the new propellant formulation by using EXPLO5_V6.03 software. The kinetic parameters of the studied samples were determined by using isoconversional methods. The results proved that TNEF melts at 126.7 °C and has a maximum decomposition peak at 210.2 °C. The prepared NC-TNEF did not show any endothermic peak and its exothermic peak was at 204.6 °C, which means that a composite might be formed during the mixing of TNEF with NC. The activation energy of the prepared NC-TNEF was in the range of 184-190 kJ mol^{-1}. NC-TNEF has higher performance and lower hazard compared with the double base propellant.

Solid propellants have a wide range of applications in tactical rockets, space launcher boosters and even amateur hobby rockets.[1] Solid rocket propellants divided into two categories: homogenous (double-base) propellants and heterogeneous (composite) propellants. Double-base propellants (DBP) which are commonly consists of the nitrocellulose (NC) as a binder plasticized by the nitroglycerine (NG) are considered as a one of the oldest solid propellant families which was developed as a result of the development of propulsion.[2] Within the time and during storage of the DBP, several physical and chemical processes take place in the propellant grains which included (the consumption of the stabilizer, migration, evaporation and decomposition of NG, etc.). The stability and the performance of propellants were affected and changed due to these processes and might cause a self-ignition for the propellants.[3] The researchers are working on solving the NG decomposition problems and it's high impact sensitivity.[4] The possibility of addition of some additives such as aluminum or nitramines (RDX, HMX, etc.) was studied.[5] Researches nowadays are focused on the synthesis of new green safe energetic materials that can replace NG in DBP to overcome the over-mentioned problems, and to enhance the energetic characteristics.[6] 2,2,2-Trinitroethanol (TNE) which is easily synthesized through a Henry reaction,[7] is one of the interesting starting material for preparation of large number of compounds.[8] 2,2,2-trinitroethyl formate (TNEF) is an interesting HEDOs. It was firstly prepared in 1967,[9] recently it was synthesized by other methods.[10] It has been used in various energy materials.[11] It has oxygen balance of (ΩCO_2) of 10.1 %, impact sensitivity of 5 J and friction sensitivity of 96 N.[10b] TNEF has lower sensitivities, higher density and oxygen balance than NG and has not been studied in any propellant formulation yet.

In addition, the investigation of the thermal behavior and decomposition kinetics of the energetic materials are necessary to find suitable new materials. The most common thermal analysis techniques such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been used to study the decomposition kinetics of many energetic materials.[12] Although TNEF is a new interesting HEDO, but it has not been thermally studied yet. In this work, synthesis and characterization of TNEF have been presented. A propellant formulation (NC-TNEF) have been prepared. The thermal behavior and decomposition kinetics of the individual NC and TNEF in addition to NC-TNEF were studied using TGA and DSC techniques. The kinetic parameters of the samples were determined by using different isoconversional methods for calculation.



Scheme 1. Synthesis of TNEF.

TNEF has been successfully synthesized from TNE and chloroform by using anhydrous Iron trichloride as a catalyst. It was characterized by ^{1}H, ^{13}C, and ^{14}N NMR and FTIR and compared with the reference.[10b] The results showed highly synthesized purity of the TNEF. NC (13.15% N) was provided by Nitrochemie Aschau GmbH.SEM results showed that the long fibers of NC were changed to the sheet form after recrystallization from acetone solution. The fibers were bonded together and were formed a homogeneous surface that took the shape of its mold after the casting process as shown in Figure 1b. Colorless hexagonal rods (60-200 µm length and 30 µm thickness) crystals of the TNEF were obtained from the preparation process (Figure 1c). Figure 1d shows a clear homogeneity of NC matrix with TNEF in the prepared propellant sample. The crystals of the oxidizer and the NC fibers are mixed

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together with a smooth colorless surface. This result may clarifies the homogeneous and smokeless burning process of the propellant recorded by high-speed camera as shown in Figure 2.

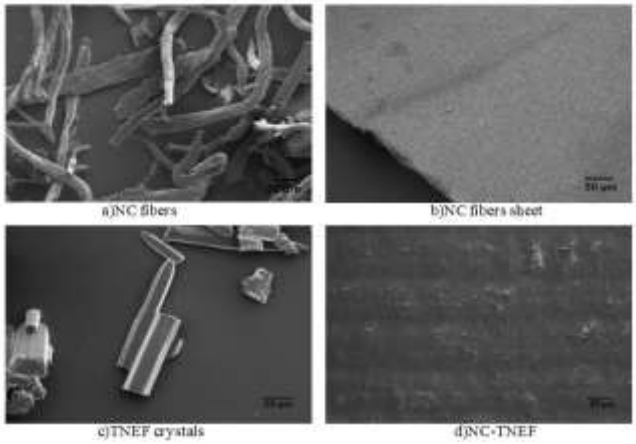

Figure 1. SEM of the oxidizer, NC and the new formulation (NC-TNEF)

Figure 2. Burning of the prepared formulation

TG/DTG thermograms of NC-TNEF under four different heating rates 2, 4, 8, and 16 ℃ min^{-1} was presented in Figure 3. The thermal decomposition of NC occurs in one sharp step, while the TNEF has a higher decomposition temperature than NC matrix (see SI). The TG/DTG thermogram of the NC-TNEF showed a controlled one-step thermal decomposition reaction with higher decomposition temperature than pure NC, which improves the thermal decomposition temperature of the new smokeless propellants compared to NC. The characteristic parameters of NC, TNEF and NC-TNEF are listed in Table 1 shows the effect of increasing the heating rate on the thermal behavior of the studied sample. Conventional Kissinger method was applied to calculate the kinetic parameters (see SI). The activation energies of NC, TNEF and NC-TNEF were 187.5, 198.4 and 190.7 kJ mol^{-1} respectively. Also, Ozawa and Flynn–Wall (OFW) developed an isoconversional calculation method to calculate the activation energy (E_a) at each fraction conversion

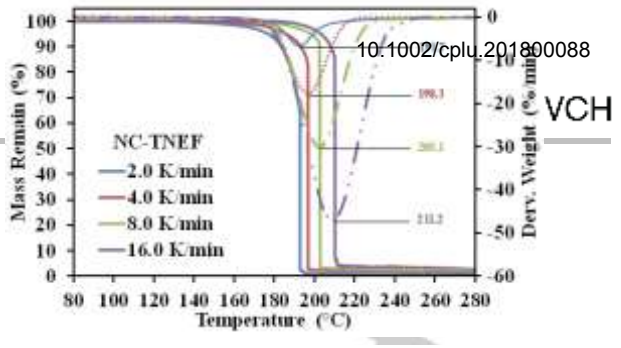

Figure 3. TG/DTG thermogram of the new formulation

(α) using nonisothermal data.[13] The E_a of NC is varied from step to step of conversion with mean value of 182.2 kJ mol^{-1}, while TNEF showed a higher value of activation energy with mean value of 192.6 kJ mol^{-1}. Figure 4 shows the activation energy at each step of conversion α for the studied samples.

DSC was used to determine the thermal behavior of the studied samples at 5 °C min^{-1}. Figure 5 shows one exothermic decomposition peak at 202.3 °C for the NC matrix. Otherwise, TNEF shows a small endothermic melting peak at 126.7 °C and an exothermic decomposed peak at 210.2 °C. Which are very close to the value of melting temperature (127.6 °C) that determined by Hill *et al.*[9] NC-TNEF showed only one exothermic peak at 204.6 °C. This result indicates that a new homogenous hydrogen-bonded complex of nitrocellulose and the oxidizer might be formed as a result of the dissolving of NC and the oxidizer in a selected solvent, followed by the evaporation of the solvent. Brodman et al stated that NC makes a chemical complex by mixing it with RDX or HMX,[14] also a π complex intermediate was formed between diphenyl amine and NC due to the high free-radical intensity possessed by the propellant composition.[15] Sovizi et al [16] stated that the decomposition parameters might be affected by the particle size of NC and the maximum decomposition peak temperature of micro-NC at 5 °C min^{-1} was 201.8 °C, which is very close to our result at the same heating rate. The results of DSC proved that the thermal behavior of TNEF has been changed completely due to its mixing with NC, which proof the advantage of using TNEF as oxidizer with NC.

Table 1. Characteristic parameters of the TG/DTG of NC, TNEF and NC-TNEF

Material	β [a] [°C.min^{-1}]	TG curves T_{ot} [b] [°C]	TG curves T_i [d] [°C]	TG curves % mass loss [f]	DTG peaks T_p [e] [°C]	DTG peaks T_{oe} [c] [°C]
NC	2.0	179.74	183.19	99.74	187.57	198.81
	4.0	186.02	189.78	99.27	193.69	212.44
	8.0	193.75	196.85	99.53	199.76	220.54
	16.0	195.79	202.34	98.96	207.28	239.68
TNEF	2.0	168.66	180.37	99.62	196.87	203.46
	4.0	174.27	187.41	99.14	203.46	218.57
	8.0	181.11	194.16	98.53	209.78	231.28
	16.0	187.96	201.75	97.98	216.21	246.94
NC-TNEF	2.0	179.81	188.04	99.13	191.69	201.52
	4.0	192.29	195.63	98.75	198.27	214.68
	8.0	199.53	202.71	98.09	205.08	225.35
	16.0	204.01	208.32	97.36	211.21	241.87

[a] heating rate. [b] onset temperature of decomposition. [c] onset temperature of the end decomposition. [d] initial thermal decomposition temperature. [e] the peak temperature of mass loss rate. [f] from initial temperature to end temperature of DTG peak

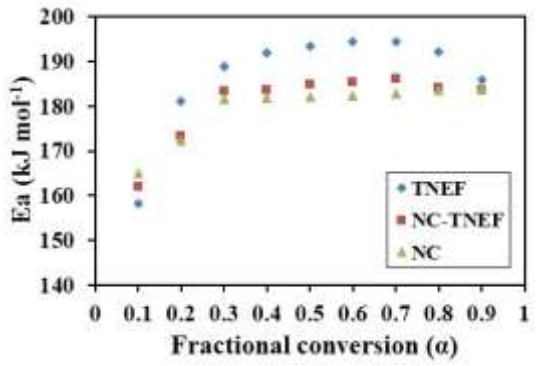

Figure 4. Activation energies at each α using OFW method

The impact and friction sensitivities of TNEF have values of 5 J and 96 N respectively at 50% probability of initiation. These results proved that TNEF has low sensitivity compared with NG. Moreover, the specific impulse calculated by EXPLO5 V_6.03 of the prepared NC-TNEF is 257.4 s that is much higher than the traditional DBP based on NC and NG. These results proved that replacement of NG by TNEF leads to decrease the hazard of the DBP and increase the specific impulse.

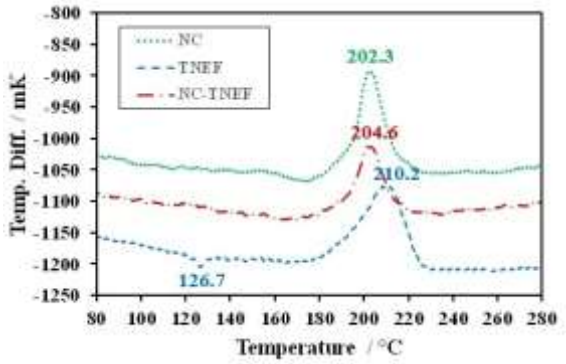

Figure 5. DSC thermogram of the studied samples at heating rate of 5°C min^{-1}

2,2,2-trinitroethyl formate is a new interesting HEDO that can be easily prepared as a powder on comparing with the dangerous liquid NG. A new propellant formula based on TNEF with NC was prepared. The SEM photos proved a good homogeneous mixing of TNEF with NC. Smokeless homogenous burning process was noticed by the high-speed camera. The thermal study proved that the prepared propellant NC-TNEF has a maximum decomposition peak temperature at 204.6 °C, which is higher than that of NC. The results proved that a new composite might be formed during the mixing process. The kinetic study showed activation energy of TNEF in the range of 193-198 ± 0.4 kJ mol^{-1}, while it was 185-191 ± 0.4 kJ mol^{-1} for NC-TNEF propellant. The new oxidizer TNEF has a much lower sensitivity than NG in addition to the high specific impulse of its propellant composition. These results confirm that TNEF could be used to replace the NG in the smokeless double base propellant and its performance should be studied experimentally.

Experimental Section

Preparation of smokeless double-base propellants formulation

Dried NC (at 60 °C for three days) was dissolved in a sufficient amount of acetone for 40 minutes at room temperature. TNEF was added in three portions to the solution of NC for 30 minutes during mixing (150 rpm). Because of the acetone high volatility, few ml of acetone should be added during the mixing process to keep the viscosity of the mixture at the same level. The prepared propellant samples were poured in a specific mold and the solvent was evaporated in a vacuum oven at 50 ±2 °C to drive out the entrapped air. The weight percentage of the prepared samples were 50 wt.% of TNEF and 50 wt.% of NC matrix.

Acknowledgements

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Keywords: HEDOs • TNEF • NC-TNEF • Thermal decomposition • Isoconversional methods

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COMMUNICATION

Smokeless safe propellants: The preparation and thermal study of the new smokeless, safe and high performance propellant formulation based on new high-energy dense oxidizer and nitrocellulose are reported. The new propellants formulation show remarkable properties: high specific impulse, high activation energy, very good homogeneity and thermal stability.

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Page No. – Page No.

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