

## Supplementary Information

### 1. TNEF Characterization

The new promising oxidizer (TNEF) was characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  NMR spectroscopy. The  $\text{CH}_2\text{C}(\text{NO}_2)_3$  singlet moiety in the  $^1\text{H}$  NMR spectra can be determined at  $\delta = 5.53$  ppm in  $[\text{D}_6]\text{acetone}$ . The methylene groups carbon resonances ( $\text{CH}_2$ ) could be observed at 63.9 ppm, while the carbon atom of the formate group was identified at 113.3 ppm and the trinitromethyl groups  $\text{C}(\text{NO}_2)_3$  at 125.5 ppm in the  $^{13}\text{C}$  NMR spectra. The nitrogen atom of  $\text{C}(\text{NO}_2)_3$  group was found at  $-33.3$  ppm in  $^{14}\text{N}$  NMR spectra. The elemental analysis showed good results for TNEF ( $\text{C}_7\text{H}_7\text{N}_9\text{O}_{21}$ ,  $M_{\text{wt.}}=553.18$  g mol $^{-1}$ ) that found (C 15.11, H 1.34, N 21.56 %), which are quite near to the calculated values (C 15.20, H 1.28, N 22.79 %).

The vibrational analysis (IR spectra) of TNEF showed the characteristic asymmetric  $\text{NO}_2$  stretching vibrations at 1585 (vs)  $\text{cm}^{-1}$ . The C–H stretching vibrations were found at 2957 (w)  $\text{cm}^{-1}$  and the  $\text{CNO}_2$  at 855 (w)  $\text{cm}^{-1}$ , where, (vs = very strong), and (w = weak).

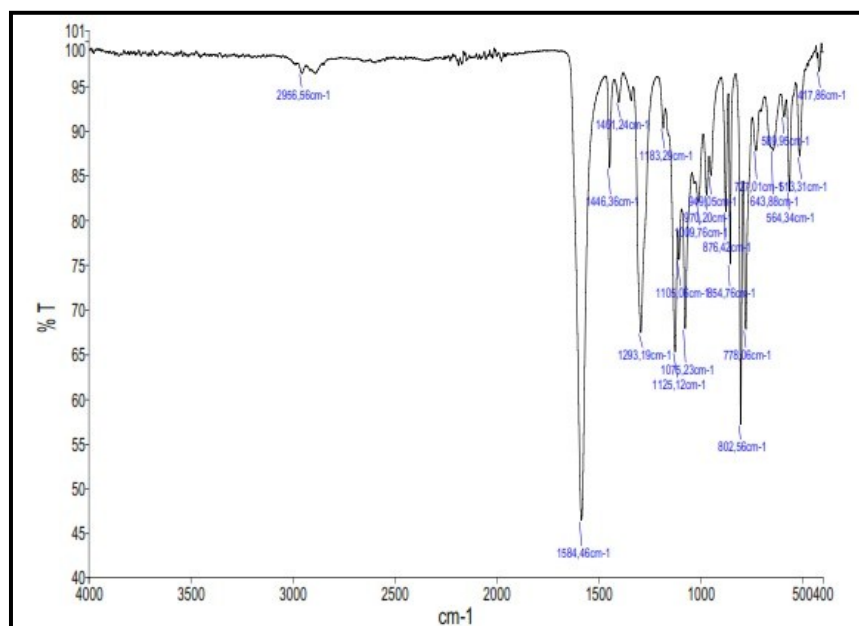


Fig. 1 FTIR of 2,2,2-trinitroethyl-formate (TNEF)

### 2. Kinetic analysis

The kinetic triplets which are the activation energy ( $E_a$ ), pre-exponential factor ( $A$ ) and kinetic model ( $f(\alpha)$ ) represent the kinetic analysis. For complete description of the kinetics, these three kinetic parameters should be determined for each reaction step. Nowadays, a large number of analytical methods that can be used to determine the kinetic parameters of distinct solid-phase reactions evaluation are available. The kinetic parameters can be determined either isothermally or nonisothermally by using two main methods which are: Isoconversional (model-free) and model-fitting methods.

### Calculation of the activation energy:

The activation energy ( $E_a$ ) of the exothermic decomposition reaction of the prepared propellants samples can be calculated by easy way using Kissinger's method.

$$-\frac{E_a}{R} = \frac{d \ln \left( \frac{\beta}{T_p^2} \right)}{d(1/T_p)}$$

Where  $\beta$  is the heating rate and  $T_p$  is the DTG peak temperature at that rate. By plotting of  $\ln(\beta/T_p^2)$  versus  $1/T_p$ , the activation energy can be calculated from the slope of this straight line. Such rough temperature integral approximation may cause an inaccurate calculated values of  $E_a$ .<sup>1</sup> More accurate equation was presented according to Starink<sup>2</sup> for  $E_a$  calculation which is commonly called the Kissinger–Akahira–Sunose (KAS) equation:<sup>3</sup>

$$\ln \left( \frac{\beta_i}{T_{\alpha,i}^{1.92}} \right) = \text{const} - 1.0008 \frac{E_a}{RT_{\alpha}}$$

Ozawa and Flynn–Wall (OFW) used a nonisothermal data and developed an isoconversional calculation method (commonly referred to as the OFW method), in which taking the logarithm of the nonisothermal rate law to give the following equation:<sup>4</sup>

$$\log g(\alpha) = \log \frac{AE_a}{\beta R} + \log \int_{\frac{E_a}{RT}}^{\infty} \frac{e^{-\frac{E_a}{RT}}}{\left(\frac{E_a}{RT}\right)^2} d\frac{E_a}{RT}$$

By substitution using Doyle's approximation:<sup>5-7</sup>

$$\log \int_{\frac{E_a}{RT}}^{\infty} \frac{e^{-\frac{E_a}{RT}}}{\left(\frac{E_a}{RT}\right)^2} d\frac{E_a}{RT} \approx -2.315 - 0.4567 \frac{E_a}{RT}$$

Then OFW equation can be written as:

$$\log \beta = \log \frac{AE_a}{g(\alpha)R} - 2.315 - 0.457 \frac{E_a}{RT}$$

### **Ref.:**

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