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Thermal-spectroscopic characterization of acetone peroxide and acetone peroxide mixtures with nitrocompounds

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Abstract Triacetone triperoxide (TATP), also known as acetone peroxide, is a powerful homemade energetic compound, highly unstable and not detectable by traditional detection technologies. The calorimetric profiles of TATP mixtures with TNT, ammonium nitrate, and nitroguanidine were evaluated and compared to pure materials. Raman spectroscopy was used to identify possible interactions between mixture components that may arise on contact. Typical results show a shift of the TATP decomposition temperature to higher temperatures, as well as decomposition of the nitrocompound initiated by TATP decomposition. The vibrational spectra were used as spectroscopic signatures for these mixtures, which can be used to understand detection challenges and for the development of desensitization approaches.

Keywords Thermal characterization · Spectroscopic characterization · Triacetone triperoxide · Acetone peroxide mixtures · Nitrocompounds

Introduction

In 2001, Richard Reid was arrested after attempting to detonate inside an aircraft a mixture of TATP and pentaerythrol tetranitrate (PETN) hidden in his shoes. His plan failed because apparently the sole of his shoes became wet, apparently deactivating the mixture. In December 2009, Nigerian national Umar Farouk Abdulmutallab tried to ignite an energetic device on Delta Airlines Flight 253 shortly before landing on Christmas day. The failed terrorist attempt also used PETN, this time hidden in a condom-like bag just below his torso, and a syringe filled with an injectable liquid intended as a secondary, detonating compound.

Worldwide terrorist activity has led to an elevated concern about national and international security [1]. Special interest has been placed in developing detection technologies for the early identification and response to threats. These threats more commonly include homemade energetic compounds assembled into improvised devices rather than traditional implements. At the same time, the increase in terrorism is fueled by the development of new energetic materials and methods for the combination of commercial explosives with domestic fabrication materials into improvised devices.

Often, the molecular interactions between the components of such mixtures are said to sensitize or desensitize an energetic material, changing its activation energy and decomposition behavior. Additionally, when using vibrational spectroscopy detection techniques, the resulting signatures may blend with non-energetic materials additives, masking the vibrational markers. The current research considers the scenario in which commercial energetic materials are blended with homemade compositions to modify their sensitivity or to conceal them for later use.

Peroxide-based energetic materials have attracted increased interest in recent years, mainly because they are widely used all over the Middle East and have recently been used in domestic attacks, such as on the mass transportation system in London (2005). TATP materials are easily prepared from very accessible materials for

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"recreational" purposes, as well as for criminal intentions. Peroxide based energetic materials bring new challenges to defense and security personnel; they are not easily detected by conventional methods of detection because they do not contain nitrogen as a constituent element. Therefore, there is great interest in studying the properties of TATP based explosives [2, 3] and their characterization, detection and discrimination from non-energetic materials.

The objective of this study was to report on the comparison of thermal properties of TATP with respect to better-known energetic materials, such as TNT and PETN. It is expected that this research will assist in the assessment of the reactivity of these materials. Also, the interaction of TATP with other known energetic materials, such as ammonium nitrate, was studied to report the spectroscopic signature of these mixtures and their potential reactivities.

Experimental

Materials

Nitroguanidine (NQ) and 2,4,6-trinitrotoluene (TNT) were acquired from commercial sources. PETN was obtained from synthesis according to current literature [4–6].

Acetone and hydrochloric acid (HCl, 1N), hydrogen peroxide (H_2O_2) and dichloromethane were used as part of the study. Synthesis of the TATP was done following the general preparation of cyclic peroxides. A white crystalline product was obtained, filtered and washed with distilled water. Recrystallization of the product was then carried out in dichloromethane. The identity of the material was confirmed by gas chromatography with an Agilent 6890 gas chromatograph coupled to a 5893 mass selective detector (HP-5 MS capillary column with 5% phenyl methyl siloxane, a length of 30 m, a 250 μm diameter and 0.25 μm of film thickness). The TATP was dissolved in dichloromethane until needed.

Methods

A model Q10 Differential Scanning Calorimeter (DSC, TA Instruments, New Castle, DE) connected to an ultra pure nitrogen gas flow was used for the experiments. High-pressure capable, hermetic seal pans were used for the DSC experiments and the samples were sealed under a nitrogen flow to maintain an inert atmosphere. The total mass was kept between 1 and 3 mg. For the kinetics experiments, sample sizes were maintained within 0.1 mg of each other. A heating rate of 5 °C min^{-1} was used for all thermal studies of highly energetic materials (HEM) samples. The DSC was calibrated with respect to temperature and enthalpy with indium (NIST traceable standard; m.p. 156.598 °C).

The activation energy (E_a) for the decomposition process was calculated according to order independent, variable heating rate kinetics. This same method was applied to differential thermal analysis (DTA) by Kissinger [7]. Ozawa then extended the applicability of this method to DSC and TGA studies [8]. The Kissinger method estimates the activation energy from the plot of the heating rate versus peak transition temperature according to Eq. 1:

$$\ln\frac{\beta}{T_\mathrm{p}^2} = \ln\left(\frac{AR}{T}\right) - \left(\frac{E_\mathrm{a}}{RT_\mathrm{P}}\right) \tag{1}$$

where β is the heating rate, T_p is the temperature at the peak of the transition and R is the ideal gas law constant. From this relationship, the activation energy can be obtained from the slope of the plot, and the frequency factor (A) is derived from the intercept. This method was selected because it has been widely applied, is the basis of an ASTM method to characterize reaction hazards of energetic materials and allows the comparison of the results obtained to well established literature values of standard materials, such as TNT and PETN [9, 10]. Dynamic experiments were run at heating rates of 5, 10, 15, and 20 °C min^{-1}.

A model RM1000 Raman microscope system (Renishaw, Inc., Hoffman Estates, IL) equipped with a Leica microscope and a NIR laser system (Process Instruments Inc., Salt Lake City, UT) operating at 785 nm was used to obtain the spectra of HEM neat samples and mixtures. The Raman shift spectra were obtained in the range of 200–3,200 cm^{-1}. The system was calibrated using a silicon single crystal sample as an external standard by measuring the vibration at 520.6 cm^{-1}. Three scans were collected for each sample with an integration time of 30 s.

Results

Differential scanning calorimetry

DSC thermograms of TATP presented an average melting temperature of 85.37 °C. The enthalpy of the transition was of 95.6 J g^{-1} (endothermic transition), which was lower than previous reports (110 J g^{-1}) suggesting the presence of small amount of impurities in the TATP samples used for this study [11, 12]. The preparation used typically results in a mixture of cyclic acetone peroxide products, including the cyclic dimer diacetone diperoxide (DADP) and in some instances even the tetramer can be produced [13].

The decomposition process of TATP had an onset temperature of about 170 °C (at 5 °C min^{-1}) and reached a maximum heat release at 193 °C (100° lower than TNT).

The exothermic decomposition had an enthalpy of 2,957 J g^{-1} and the decomposition transition displayed a shoulder that developed into a small peak at higher heating rates, suggesting that the decomposition occurred stepwise. The measured energy released by TATP decomposition compared favorably to the exothermic behavior of TNT.

Table 1 summarizes the DSC data for TNT, TATP, NQ, DNT, RDX, and PETN. The thermal data was obtained at 5 °C min^{-1} for all samples. The order for exothermic energy released at decomposition was found to be TNT > RDX > TATP > PETN > 2,4-DNT > NQ. It was noticeable that TATP has a decomposition enthalpy comparable to TNT and RDX, but had the lowest peak decomposition enthalpy.

The overlay of the decomposition peak of TATP at different heating rates (HR, β) is shown in Fig. 1. At 5 °C min^{-1}, the decomposition demonstrated a sharp peak, but at higher heating rates, however, a shoulder developed suggesting again that the decomposition may have occurred over more than one step. The peak temperature was monitored and plotted against heating rate, and the plot was fitted into Eq. 1 to obtain the activation energy according to the Kissinger method.

Figure 2 summarizes the data for determination of activation energy of the studied HEM. The four materials evaluated were separated into two groups: one decomposing near 200 °C (TATP and PETN), and the other that decomposed at 300 °C (DNT and TNT). Table 2 presents the activation energies for the materials evaluated with TNT, DNT, and PETN. These values agree with reported values within 10–18%. However, the activation energy of TATP was 50% lower than the reported value, with the value found in the current study being more consistent with a highly reactive material with a high sublimation rate at room temperature (RT). The value previously reported for TATP was very similar to the values of PETN, TNT, and RDX, materials known as secondary energetic materials and with implicit higher activation energies. The observed discrepancy, however, suggests numerous possibilities. First, if impurities are present as suggested by the lower melting temperature it can be expected that some reduction in the activation energy was due to the interaction with impurities. However, impurities should not be responsible for a reduction of half the expected value. Also, it is worth mentioning that it is rather normal to find considerably different values for the calculated activation energies. Brill and James discuss the origin of these differences in their study [14]. The thermal decomposition process can be divided in three main steps: induction, acceleration and decay. Values obtained during the induction or bond breaking step are typically higher. However, the transition is not easily appreciable by dynamic methods, resulting in high variability in the data obtained. Most of the values reported were found to be representative of the acceleratory phase using the maximum decomposition rate (peak of the exothermic transition). Values that are slightly lower during this phase are an indication of autocatalysis. The third phase is known as the decay phase and is highly dependent on the concentration of decomposition products that help catalyze the process to completion. For the current study, the activation energy for TATP at the peak decomposition temperature was 72.2 kJ mol^{-1}. However, when the measurement was taken at the onset of decomposition, the value was found to be 106.3 kJ mol^{-1}. This value indicates that the decomposition was autocatalyzed by the products formed during the first phase.

Table 1 DSC results for studied highly energetic materials

HEM	T_m/°C	H_m/J g^{-1}	T_{onset}/°C	T_{dec}/°C	H_{dec}/J g^{-1}
TNT	80.80	96.79	306.88	312.71	3,486
2,4-DNT	70.17	124.20	290.38	307.55	1,695
NQ			226.04	228.73	688
PETN	129.30	85.58	136.92	199.63	2,163
RDX	202.00	105.00	204.00	213.00	3,327
TATP	83.93	106.30	170.00	193.00	2,957

T_m melting temperature, H_m enthalpy of melting, T_{onset} onset for the decomposition, T_{dec} peak of the decomposition transition, H_{dec} Enthalpy of decomposition, *HEM* high energetic material

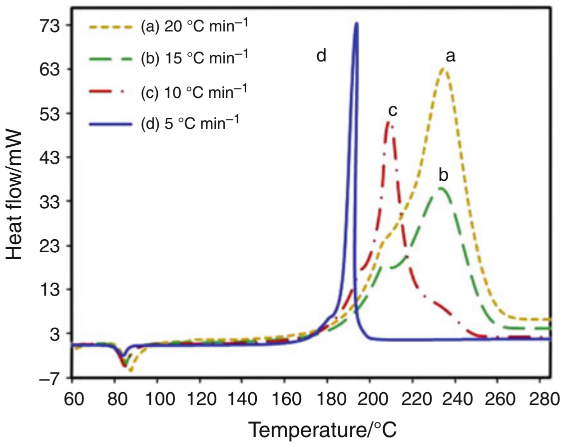

Fig. 1 Overlay of decomposition peak of TATP at different heating rates: *a* 20 °C min^{-1}; *b* 15 °C min^{-1}; *c* 10 °C min^{-1}; *d* 5 °C min^{-1}

The TATP–nitroguanidine system

Nitroguanidine (NQ) is considered a nitrimine or primary nitramine. NQ has many applications as an additive for gunpowder and propellants. It is also considered a low performance energetic material [12]. The objective of mixing TATP with NQ was to study the effect of the amino groups on the peroxide groups of TATP. The Raman

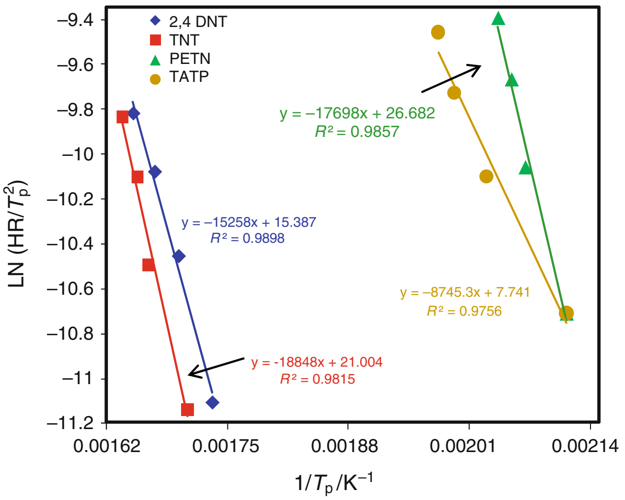

Fig. 2 Plot of heating rate vs. peak transition temperature for energetic materials. This representation is used to calculate the activation energy for decomposition. (HR: heating rate; T_p: peak transition temperature; slope: $-E_a/R$)

Table 2 Activation energies for energetic materials

Materials	Activation energy (peak decomposition) kJ mol^{-1}	Data correlation R^2	Literature values kJ mol^{-1}
TNT	156.7	0.982	144[a]
Onset	165.5	0.976	
2,4-DNT	126.9	0.989	
Onset	132.4	0.966	
PETN	147.1	0.985	175 [9]
Onset	72.9	0.948	
TATP	72.7	0.976	153 [2]
Onset	106.3	0.962	

[a] Los Alamos Center for dynamic material properties explosive properties data series

spectra of a blend of 40% (w/w) NQ and TATP is presented in Fig. 3a. The spectra have components of both TATP and NQ, suggesting that the sampled area was representative of the total mixture. The presence of molecular interparticle interactions in the binary mix were not detected using Raman scattering. The DSC of the decomposition process of this blend is included in Fig. 3b. The decomposition of the pure substances were characterized by sharp exothermic peaks at 195 °C (TATP) and 235 °C (NQ). The thermogram of the blend was found to have a melting transition close to 90 °C. This transition contained two peaks, which suggested that NQ was dissolved in TATP. Neat samples of nitroguanidine did not present melting transitions in DSC, despite that the peak for this transition was expected at 247 °C. The decomposition transition consisted of a wide peak extending from 180 to 240 °C, and a region with two maxima at 200 and 220 °C.

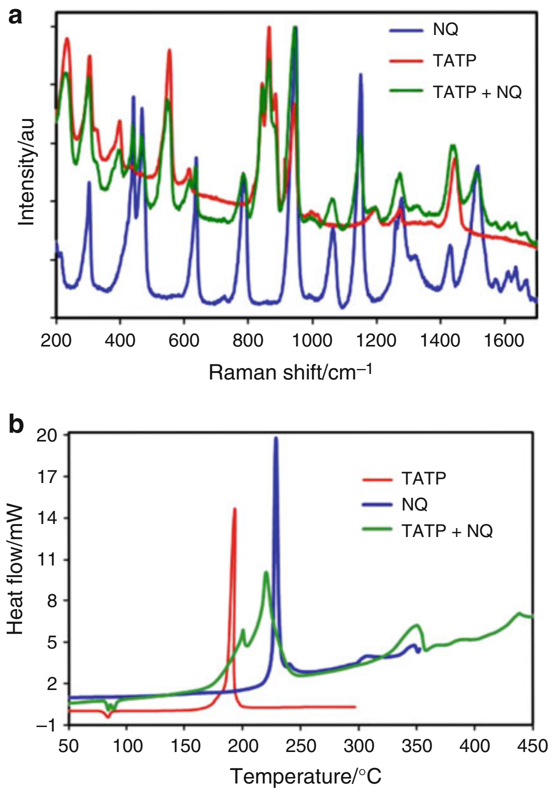

Fig. 3 **a** Raman spectra of TATP, NQ and binary mix of 40% (w/w) NQ + TATP. Mixture was solidified from melt. Parameters: 3 scans, 30 s, 785 nm laser excitation; **b** Comparison of the DSC thermograms of TATP, NQ and 40% NQ mix. Parameters: 2–3 mg sealed in a high pressure pan, 5 °C min^{-1}

There was a secondary exothermic peak at 350 °C, which was not observed in the thermogram of pure TATP or NQ, suggesting that it could be due to the decomposition of a species formed during the exothermic process at a lower temperature.

The TATP–TNT system

The chemistry of TNT is characterized by the strong conjugation derived from having three electron withdrawing nitro groups in the benzene ring, which causes an enhancement of the reactivity of the methyl group. The hydrogen atoms of the methyl group have an acidic character, making this methyl group a nucleophile under special circumstances [12]. TNT is very popular as a precursor for polynitroarene synthesis. The important nitro-HEM was blended with TATP to study if the methyl group could interact with the peroxide groups of TATP.

Figure 4a contains the Raman spectra of a 50% mix of TATP and TNT (top to bottom). The resultant spectrum was essentially a composite of the pure material spectra. The spectrum of the binary mix, however, presented wider

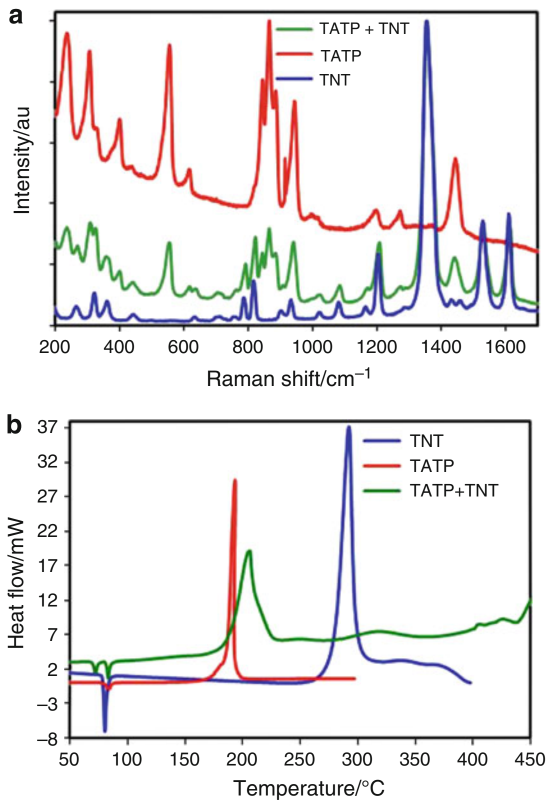

Fig. 4 **a** Raman spectra of AN, TATP and mixture of 35% AN + TATP. Samples were solidified from melt. Parameters: 3 scans, 30 s and 785 nm laser excitation; **b** Comparison of the DSC thermograms of TATP, AN and mix containing 35% AN (w/w). Parameters: 2–3 mg sealed in a high pressure pan, 5 °C min^{-1}

bands in the 768–900 cm^{-1} and 282–334 cm^{-1} wavenumber ranges as a result of the combination of bands from each component. However, significant shifts or broadening of bands that could indicate a strong intermolecular interaction between the two HEM were not observed. The DSC thermogram (Fig. 4b) showed two melting transitions in the 70 to 80 °C region, which were lower than the melting transition of TNT (~80 °C). The decomposition signal consisted of a wide peak from 180 to 225 °C and only displayed one maximum at 206 °C, indicating that all the solid decomposed almost simultaneously after initiation. There was, however, a small exothermic transition close to 300 °C indicating residual TNT material. The transition enthalpy was lower than any of the components, indicating that the decomposition occurred by mechanisms different from those of the pure materials.

The TATP–ammonium nitrate system

Ammonium nitrate (AN) is probably the most commonly used material in HME due to its wide availability in fertilizers. Ammonium nitrate mixtures with diesel, kerosene or No. 2 fuel oil are collectively known as ANFO, which is considered to be the most used explosive in mining and construction. AN is also known as a sensitizer used to reduce the activation energy of highly energetic materials. This fact apparently arises as a result of HNO_3 (gas) formation during the heating of AN. The mechanism of decomposition of ammonium nitrate and its role in the sensitization of nitrocompounds, such as TNT, have been studied in detail. In 1994, Oxley, et al. reported the effect of AN on nitroexplosive mixtures. In these combinations, ammonium nitrate acted as an oxidizing agent and the decomposition of AN produced the important gases HNO_3 and NH_3. These species could then attack the nitrocompounds, destabilizing the mixture and reducing the activation energy [15, 16].

The vibrational spectra of TATP blended with 35% (w/w) AN was obtained after melting and cooling (Fig. 5a, b). The spectrum of the mix was dominated by TATP vibrational signals due to the simple spectra displayed by the polyatomic anion $NO_3{}^{1-}$. The presence of AN was only marked by a small peak at 1,042 cm^{-1} ($NO_3{}^{1-}$). Moreover, this mixture exhibited the strongest intermolecular interaction, both in Raman scattering as well as in DSC studies. The AN band located at 713 cm^{-1} was shifted to 706 cm^{-1} and the strong, totally symmetric vibration of AN experience a bathochromic shift to 1,030 cm^{-1}. TATP signals also shifted indicating the presence of the strong interparticle interaction. The vibrational signature of cyclic acetone peroxides located at 943 cm^{-1} (ω_{CH_2} and $\nu_{O\text{–}O}$) appeared at 946 cm^{-1} in the binary mix with AN and the CH_2 bending at 1,444 cm^{-1} increased to 1,451 cm^{-1} in the spectrum of the blend. Tentative spectroscopic band assignments follow Pacheco-Londoño et al. [4]. Thus, TATP vibrations shifted to higher energies and AN vibrations stabilized by the interaction with TATP, decreasing in energy. A stabilizing effect was also found by Zeman and Bartei in AN-TATP mixtures [17]. The DSC thermogram of AN, TATP and the blend was also included in Fig. 5c. The thermal profile of TATP presented an endothermic transition (melting) between 80 and 90 °C, an onset for exothermic decomposition at 170 °C and the peak exothermic transition occurred at 195 °C. For AN, the thermogram showed two endothermic transitions under 150 °C and the decomposition process was located at 300 °C. The thermogram of the mixture displayed a wide exothermic transition in the temperature range where TATP decomposes rapidly. There was an exothermic peak close to 240 °C, with no further transitions that could be attributed to AN decomposition. This profile suggested a physical and/or chemical interaction between these materials. The presence of AN delays the TATP decomposition exotherm while simultaneously the presence of TATP in AN affected its thermostability. The vibrational spectra of the mixture presented shifts in

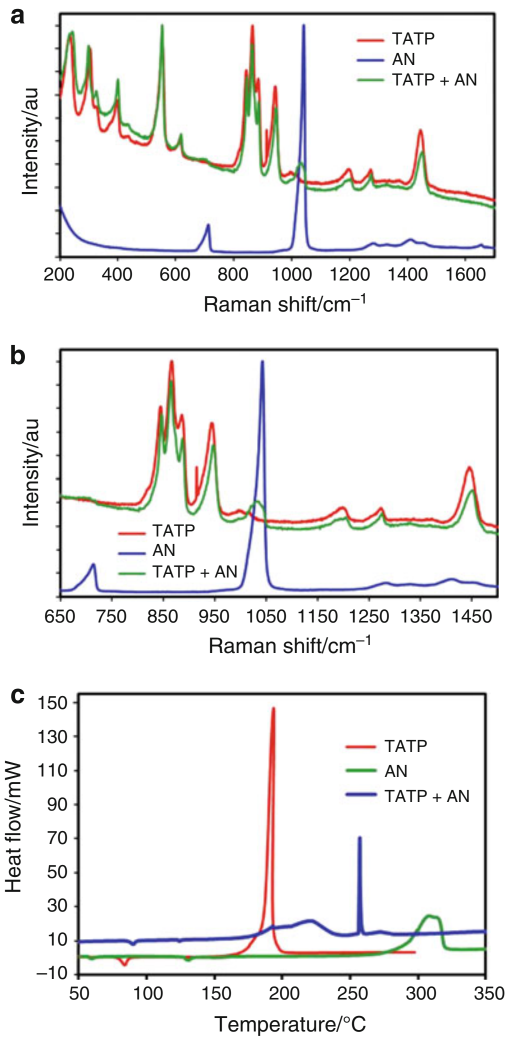

Fig. 5 **a** Raman spectra of AN, TATP and mixture of 35% AN + TATP. Samples were solidified from melt. Parameters: 3 scans, 30 s with 785 nm laser excitation; **b** Detail of region of spectroscopic evidence of intermolecular interaction between AN and TATP; **c** Comparison of the DSC thermograms of TATP, AN and the mixture containing 35% AN. Parameters: 2–3 mg sealed in a high pressure pan, 5 °C min^{-1}

characteristic bands suggesting a stronger interaction than observed for other mixtures. However, it is possible that this behavior is caused by the AN absorbing part of the heat of decomposition of TATP during melting while being consumed in the process. At 260 °C the remaining TATP decomposed violently, as indicated by a sharp exothermic peak.

Conclusions

The effect of mixing TATP with other energetic materials was studied by vibrational spectroscopy and thermal analysis. As expected, TATP had a destabilizing effect on other energetic materials. It could be assumed that, upon decomposition, the TATP decomposition products could attack the other energetic materials in the mixtures. On the AN-TATP mixture, the decomposition peak of TATP was shifted to higher temperatures. This can be indicative of a physical or chemical interaction not observed in other mixtures. This interaction reduces the thermal stability of AN while delaying the exothermic decomposition of TATP.

The Raman signatures of mixtures of TATP and nitro compounds are reported. Characteristic peaks for the peroxide bond as well and the nitro groups are maintained. Therefore, the identification and quantification of components can be attained. The characterization of vibrational spectra was used to evaluate and propose possible interactions that can result in differences in thermal stability of an AN-TATP mixture.

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