

Thermal stability of triacetone triperoxide

Robert Matyas*† and Jiri Pachman**

*University of Pardubice, Institute of Energetic Materials, Studentska 95, 532 10 Pardubice, CZECH REPUBLIC

† Corresponding address: robert.matyas@upce.cz

**Nanyang Technological University, Energetic Materials Research Centre, Nanyang Drive N1-B4a-02, 639798, SINGAPORE

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Abstract

Thermal stability of triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) was investigated by differential thermal analysis (DTA). Two main aspects have been found to influence the thermal stability of raw (not recrystallized) TATP - type of acid used for catalysis and its amount expressed here as acid to acetone molar ratio ($n_c n_a^{-1}$). The decomposition of TATP begins around 145°C when hydrochloric or nitric acid is used. Altering the $n_c n_a^{-1}$ ratio from 2.5×10^{-4} to 5×10^{-1} does not have measurable influence in case of these acids. A significant influence was however found when using sulfuric or perchloric acid. A low concentration of these two acids ($n_c n_a^{-1} \leq 1 \times 10^{-2}$) yields product that decomposes above 145°C just as seen in case of pure (recrystallized) TATP. Higher concentrations however yield TATP that decomposes during melting or even in solid phase. It was found that the lower thermal stability is a result of combination of two factors - overall residual acidity within the TATP crystals and probably acid strength. A dependency of onsets of decomposition on heating rate was found to be steeper for TATP catalyzed by sulfuric acid than for TATP catalyzed by either hydrochloric, nitric or perchloric acid.

Keywords: Triacetone triperoxide, 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP, Thermal stability, DTA.

1. Introduction

The triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) has been known for over a century now. It was first described Wolffenstein¹⁾ in 1895 and the main reason why attention is once again drawn to this explosive is that it became popular among various extremists and terrorists in Western world recently²⁾⁻⁴⁾. TATP has also been very popular among young "scientists"⁵⁾ and therefore presents material often seized by police. Our intention was to examine TATP with properties as close as possible to the material found by law enforcement groups. For this purpose we have followed synthetic procedures from extremist's web sites often mentioned by inexperienced chemists on internet discussion forums⁵⁾ and excluded purification by recrystallization. The results presented in this article summarize thermal stability studies of such "raw TATP" samples prepared using common inorganic acids using differential thermal analysis (DTA). The influence of easily obtainable organic acids is summarized elsewhere⁶⁾.

The reaction of acetone with hydrogen peroxide yields several organic peroxides and had been extensively studied in the past^{7), 8)}. The final product is always a mix-

ture of various peroxides and the resulting composition depends on the reaction conditions. Linear hydroperoxides form without acid catalysis while TATP represents the main product of the reaction in presence of an acid catalyst. The resulting product could be in dependence on reaction conditions contaminated with diacetone diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetroxane, DADP) and recently reported tetraacetone tetraperoxide (3,3,6,6,9,9,12,12-octamethyl-1,2,4,5,7,8,10,11-octaoxa-cyclododecane, TeATeP)⁹⁾⁻¹¹⁾. DADP forms as side product especially when sulfuric acid is used⁹⁾ and at higher reaction temperatures (above 10°C)¹¹⁾. A higher purity TATP has been reported when sulfuric acid was replaced with hydrochloric acid⁹⁾.

Thermal decomposition of TATP was investigated by a number of authors. Oxley et al¹²⁾ studied mechanisms of decomposition by DSC and identified decomposition products by GC/MS. DSC has also been used by Bellamy⁹⁾ who reported the stable liquid phase with melting point at 97°C and decomposition above 160°C for pure TATP.

The theoretical thermal decomposition pathway of TATP molecule was calculated by Dubnikova et al¹³⁾. A non-explosive decomposition of TATP in solutions was inves-

Table 1 The dependence of beginnings of decomposition of TATP (prepared under catalysis of various inorganic acids) on acetone to acid molar ratio n_c / n_a^{-1} (heating rate 5°C min^{-1}).

Molar ratio n_c / n_a^{-1}	Sulfuric acid	Perchloric acid	Hydrochloric acid	Nitric acid
5×10^{-1}	Decomposition starts before melting			
2.5×10^{-1}		Decomposition starts before melting		
1×10^{-1}				
5×10^{-2}	Decomposition during melting			
2.5×10^{-2}		Decomposition during melting		
1×10^{-2}			Decomposition starts above 145°C	Decomposition starts above 145°C
5×10^{-3}	Decomposition starts above 145°C			
2.5×10^{-3}		Decomposition starts above 145°C		
2.5×10^{-4}				

tigated by Bellamy⁹. The mechanism of decomposition in organic solvents at higher temperatures was investigated by Eyler et al¹⁴.

2. Experimental

2.1 TATP samples preparation

Caution: TATP is primary explosive sensitive to impact, friction, electric discharge and flame. The synthesis and handing of TATP are dangerous operations that require safety precaution for handing of primary explosives!

All “raw TATP” samples were prepared by following procedure: 14.7 ml (0.20 mol) of acetone (grade purum, supplied by Lach-Ner) was mixed with 25.5 ml (0.25 mol) of 30 % hydrogen peroxide (grade purum, supplier Lach-Ner). The acid (grade p.a., supplier Lach-Ner) in the amount as listed in the first column of Table 1 (n_c / n_a^{-1} represents acid to acetone molar ratio) was added to stirred water cooled reaction mixture. The water cooling kept the reaction mixture at temperature below 20°C . The mixture was further kept at a laboratory temperature without stirring or cooling for 24 hours. In cases when TATP did not form or formed in a low yields within the first 24 hours additional 6 days were allowed for the reaction at room temperature. The resultant precipitate was collected by filtration, washed once with distilled water, once with 1 % solution of sodium carbonate, then again five times with water (until neutral pH) and dried at room temperature. This “raw” product was not purified by recrystallization. The “pure TATP” was obtained from the “raw TATP” by recrystallization from methanol (repeated five times).

2.2 Differential thermal analysis

The thermoanalytical properties of TATP were studied using differential thermal analyzer DTA 550Ex produced by OZM Research. The 30 mg samples were tested in open glass micro-test tubes in air. The heating rates ranged from 0.2 to $20^\circ\text{C min}^{-1}$.

2.3 Determination of residual acidity in TATP

The residual acidity in TATP crystals was determined by titration. TATP was dissolved in methanol and the solution was titrated by 1.0 M tetrabutylammonium hydroxide in methanol (grade undetermined, supplied supplier Aldrich, prod. number 230189). Automatic titrator ABU 93 TRIBURETTE produced by Radiometer Copenhagen was used.

3. Results and discussion

3.1 Influence of catalyst

The decomposition behavior of TATP depends significantly on the type of the acid used as a catalyst during synthesis. This can be clearly seen from the Fig. 1 which show typical DTA thermograms of TATP prepared using the following catalysts: hydrochloric, sulfuric, nitric and perchloric acids. The heating rate 5°C min^{-1} and a static air atmosphere were used in these trials. All samples were prepared using the same amount of catalyst ($n_c / n_a^{-1} = 2.5 \times 10^{-1}$).

The melting point published for TATP ranges from 95 to 98.5°C ^{1, 7, 9, 15, 16}. This is in agreement with our findings for pure TATP (Fig. 1) and some “raw TATP” samples. The “raw TATP” however mostly begins to melt at significantly lower temperatures (just above 70°C) as can be seen from the beginning of the endothermic peak (Fig. 1). The shape as well as the onset temperature of this endothermic peak depend on the type of the catalyst and reflect the amount of side-products in TATP⁶.

The TATP samples may be divided into two groups according to their behavior after melting. The samples in the first group (catalyzed by nitric or hydrochloric acid) are stable in the liquid phase and do not show significant signs of decomposition below 145°C under the conditions of the experiment. The course of decomposition of these samples is practically identical to that of pure TATP. Their thermal behavior also does not depend on the amount of catalyst (n_c / n_a^{-1} from 2.5×10^{-4} to 5×10^{-1}) used during the preparation.

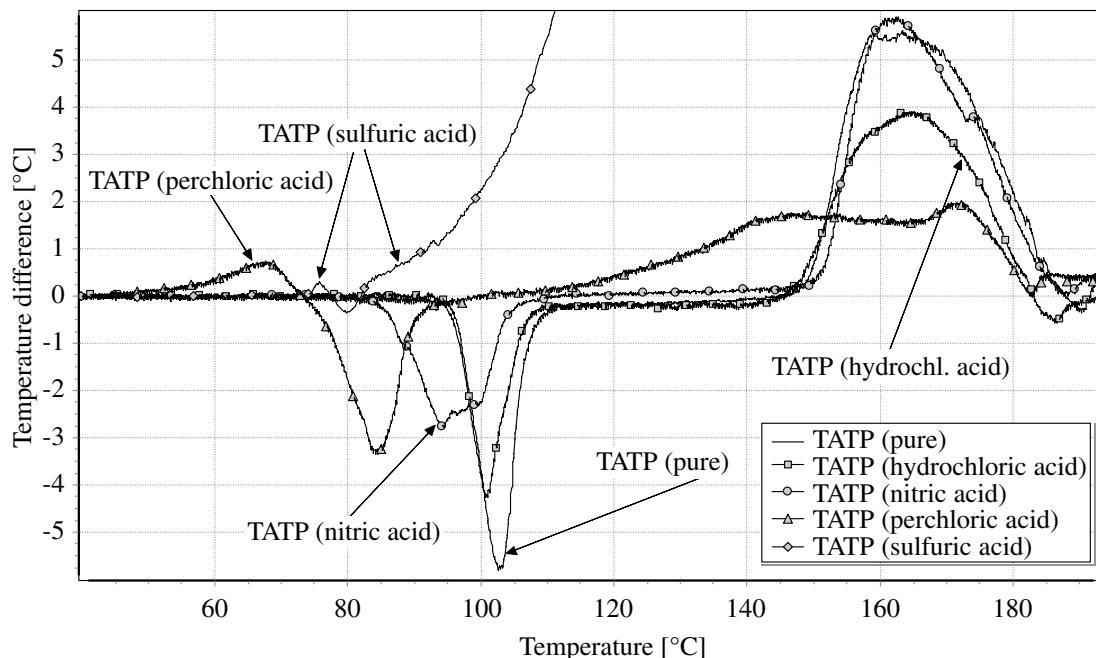


Fig. 1 DTA thermograms of TATP prepared using inorganic acids ($n_c n_a^{-1} = 2.5 \times 10^{-1}$ for all acids) as catalyst and pure TATP (heating rate $5^{\circ}\text{C min}^{-1}$, 30 mg samples and static air atmosphere).

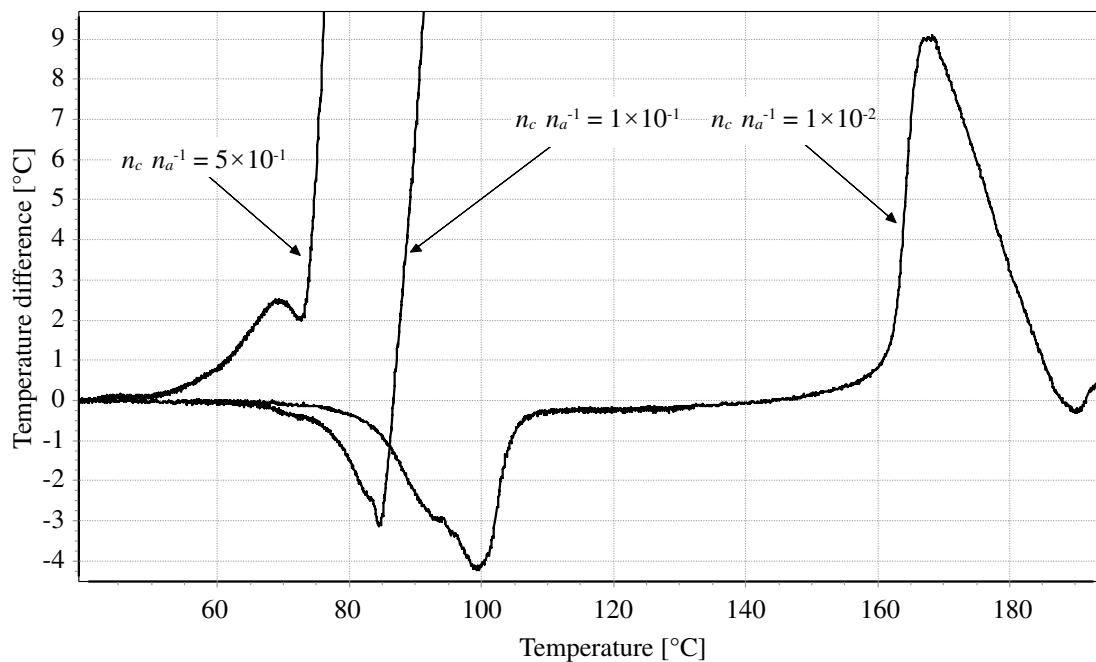


Fig. 2 DTA thermograms of TATP demonstrating the influence of the concentration of sulfuric acid in reaction mixture - $n_c n_a^{-1}$ on the thermal stability of resulting product (heating rate $5^{\circ}\text{C min}^{-1}$, 30 mg samples and static air atmosphere).

The samples in the second group (catalyzed by sulfuric or perchloric acid) generally decompose at lower temperatures and their thermal behavior depends on the amount of catalyst used. The samples prepared with low amounts of sulfuric acid ($n_c n_a^{-1} \leq 1 \times 10^{-2}$) decompose in the same way as pure TATP. Increasing the amount of sulfuric acid causes the decomposition to occur during melting ($n_c n_a^{-1} = 2.5 \times 10^{-2}, 5 \times 10^{-2}$ and 1×10^{-1}). Further increase of catalyst concentration results in decomposition from solid phase before melting ($n_c n_a^{-1} = 2.5 \times 10^{-1}$ and 5×10^{-1}). These three main types of decomposition demonstrating dependency of thermal behavior on the amount of catalyst can be seen from

Fig. 2. A similar behavior was also observed for samples of TATP obtained under catalysis of perchloric acid. The decomposition in this case begins around 145°C for $n_c n_a^{-1} \leq 1 \times 10^{-2}$, during melting in case of $n_c n_a^{-1} = 2.5 \times 10^{-2}, 5 \times 10^{-2}$ and in solid phase when $n_c n_a^{-1} = 1 \times 10^{-1}, 2.5 \times 10^{-1}$ and 5×10^{-1} . Thermograms of three main types of decomposition of TATP prepared with the use of varying amount of perchloric acid are presented in Fig. 3.

The overview of TATP samples prepared using common inorganic acids for catalysis of the reaction of acetone and hydrogen peroxide and the influence of catalyst concentration on the thermal stability are summarized in Table 1.

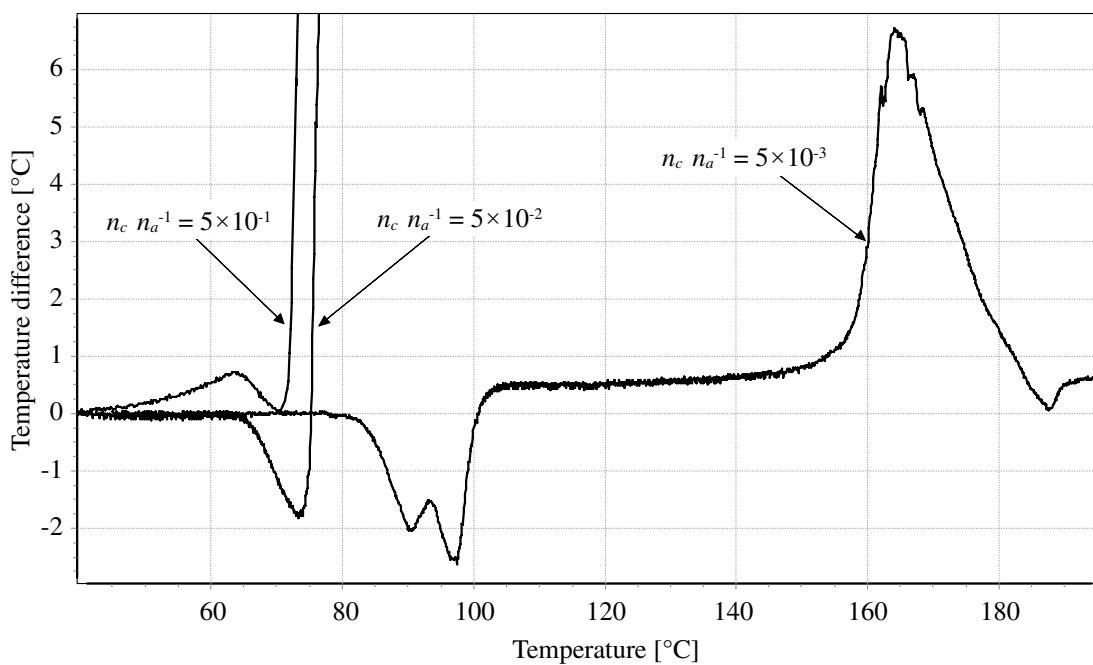


Fig. 3 DTA thermograms of TATP demonstrating the influence of the concentration of perchloric acid in reaction mixture - $n_c n_a^{-1}$ on the thermal stability of resulting product (heating rate 5°C min^{-1} , 30 mg samples and static air atmosphere).

Table 2 The average content of residual acidity (wt. %) in TATP crystals prepared using various acids at varying concentrations (molar ratio $n_c n_a^{-1}$).

Molar ratio $n_c n_a^{-1}$	Hydrochloric acid	Nitric acid	Perchloric acid	Sulfuric acid
5×10^{-1}	30×10^{-3}	82×10^{-3}	125×10^{-3}	110×10^{-3}
2.5×10^{-1}	31×10^{-3}	45×10^{-3}	42×10^{-3}	100×10^{-3}
1×10^{-1}	2.5×10^{-3}	23×10^{-3}	11×10^{-3}	13×10^{-3}
5×10^{-2}	—	—	—	12×10^{-3}

It has been assumed that the differences in decomposition behavior are related to the residual acidity inside the TATP crystals. The possible influence of free acid on the crystal surface is not probable since all samples were washed to neutral reaction after preparation. The amounts of residual acidity (in wt. %) determined by titration after dissolving the crystals are summarized in Table 2.

The amount of acidity in the samples catalyzed by nitric acid is similar to the amount of acidity found in the samples prepared using perchloric acid (Table 2). The decomposition behavior of both however differs significantly therefore not only the amount of the acid but probably also its strength influence the decomposition behavior. We assume that the acid is trapped in the crystals in the form of its aqueous solution. On the basis of published results of pKa values of aqueous solutions it is possible to sort acids in the following order with respect to their strength:



The strongest is the perchloric and weakest is the nitric acid. The order of sulfuric and hydrochloric acids depends on literature source¹⁷⁻²⁰.

In order to confirm our assumption we added 0.1 wt. % of nitric or sulfuric acid (both as 3 wt. % aqueous solutions) to the pure TATP and analyzed on DTA. The amount of acid corresponds to the amount of acidity found in samples prepared with ratio $n_c n_a^{-1} = 5 \times 10^{-1}$. The resulting thermograms are presented on Fig. 4 showing that the addition of sulfuric acid decreases the thermal stability of TATP while the addition of nitric acid in the same amount does not have noticeable effect. The broad first endo-peak on thermogram of mixture of TATP and nitric acid is caused by evaporation of aqueous solution of acid from this mixture. The same peak is present in the case of mixture of TATP and sulfuric acid but it is not so noticeable due to overlay of water evaporation and beginning of TATP decomposition.

3.2 Influence of heating rate

A various heating rates were used to see if kinetic parameters can be calculated. The samples were measured in triplicate at heating rates (β) 0.5, 1, 2, 5, 10 and $20^\circ\text{C min}^{-1}$. It was shown that TATP can be studied even in relatively large quantities and still decompose without ignition. The original intention to calculate the kinetic param-

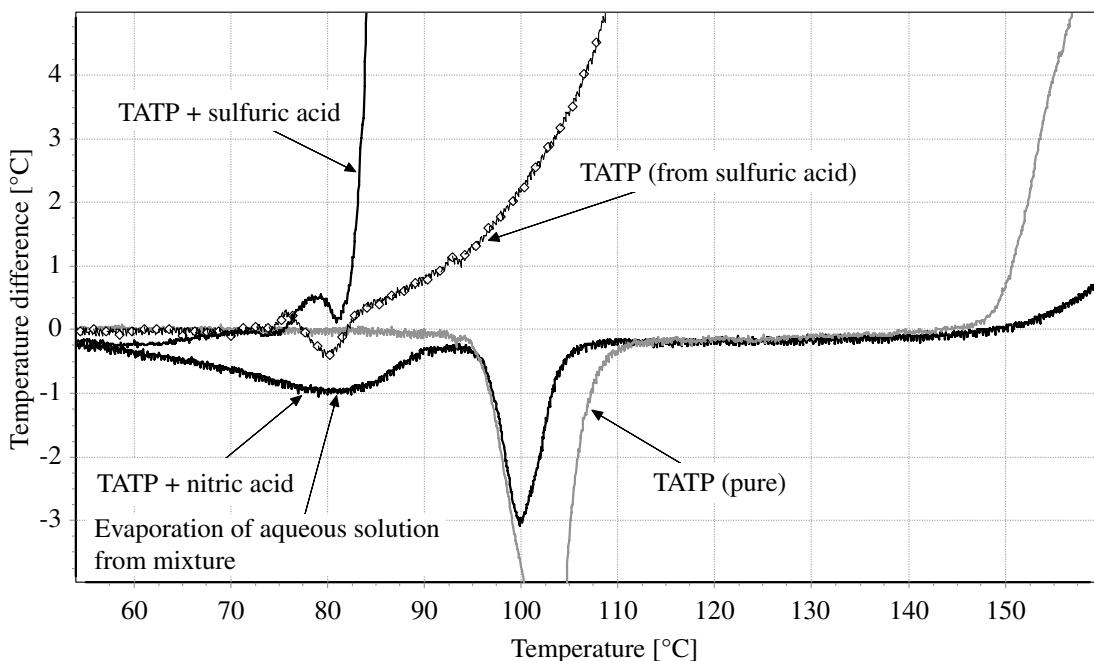


Fig. 4 DTA thermogram of the mixtures of pure TATP with sulfuric and nitric acid ($w_a = 0.1$ wt. % for both acids in form of 3 wt. % water solutions, heating rate $5^{\circ}\text{C min}^{-1}$, 30 mg samples and static air atmosphere).

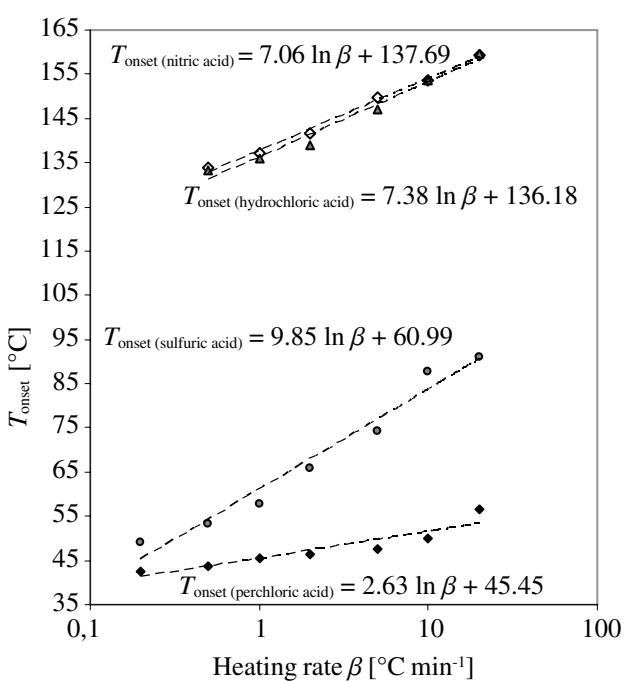


Fig. 5 Dependence of T_{onset} of decomposition on β (heating rate) for TATP prepared from hydrochloric, nitric sulfuric and perchloric acid ($n_c n_a^{-1} = 2.5 \times 10^{-1}$, 30 mg samples and static air atmosphere).

eters was however too optimistic due a complex nature of TATP decomposition behavior. It is believed that the pure TATP and carefully prepared mixtures of pure TATP with acids should be used for kinetic analysis rather than these “real material” simulating samples. The only part we have decided to include into this article are dependences of onset (T_{onset}) of decomposition on temperature. The

Figure 5 shows that the onsets of decomposition (T_{onset}) for samples prepared using hydrochloric and nitric acid are practically identical and as previously mentioned at much higher temperatures compared to the samples prepared using sulfuric acid or perchloric acid.

4. Conclusions

Thermal stability of raw TATP (not purified by recrystallization) was investigated by DTA. The type and the amount of acid used as a catalyst in TATP preparation have a major impact on its thermal stability. Decomposition of TATP starts above 145°C when hydrochloric or nitric acid is used. The thermal stability of TATP prepared using sulfuric or perchloric acid varies with the acid concentration. Increase in concentrations of sulfuric or perchloric acid during preparation results in product with lower thermal stability. The onset of decomposition of TATP may therefore vary from 50°C to 145°C for the same acid depending on concentration. The residual acidity in crystals together with acid strength was proposed as the main reasons of thermal instability of raw TATP.

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5. References

- 1) R. Wolffenstein, Ber. Dtsch. Chem. Ges., 28, 2265 (1895).
- 2) T. Michalske, N. Edelstein, M. Sigman, J. Trewhella, "Basic Research Needs for Countering Terrorism", workshop report, on-line at: http://www.er.doe.gov/bes/reports/files/NCT_rpt_screen.pdf (29. 1. 2007).
- 3) IntelCenter, "London Tube Bus Attack (LTBA) v 1.5", report, on-line at: <http://www.intelcenter.com/LTBA-PUB-v1-5.pdf> (29. 1. 2007).
- 4) D. Philpott, "The London Bombing", Homeland Defence Journal, on-line at: http://www.homelanddefensejournal.com/pdfs/LondonBombing_SpecialReport.pdf (29. 1. 2007).
- 5) R. Matyas, Grant of the Ministry of Internal Affairs of Czech Republic, no. RN 20012003003, 2002, University of Pardubice, Czech Republic.
- 6) R. Matyas, Investigation of properties of Selected Organic Peroxides, PhD Thesis, 2005, University of Pardubice, Czech Republic.
- 7) N. A. Milas, A. Golubovic, J. Am. Chem. Soc., 81, 6461 (1959).
- 8) M. C. V. Sauer, J. O. Edwards, J. Phys. Chem., 75, 3004 (1972).
- 9) A. J. Bellamy, J. Forensic Sci., 44, 603 (1999).
- 10) R. Schulte-Ladbeck, P. Kolla, U. Karst, Anal. Chem., 75, 731 (2003).
- 11) A. J. Pena, L. Pacheco-Londono, J. Figueroa, L. A. Rivera-Montalvo, F. R. Roman-Velazquez, S. P. Hernandez-Rivera, Proceedings of SPIE-The International Society for Optical Engineering, pp. 347-358, vol. 5778 (2005), Bellingham WA.
- 12) J. C. Oxley, J. L. Smith, H. Chen, Prop., Expl., Pyr. 27, 209 (2002).
- 13) F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, R. Boese, H. Itzhaky, A. Alt, E. Keinan, J. Am. Chem. Soc., 127, 1146 (2005).
- 14) G. N. Eyler, C. M. Mateo, E. E. Alvarez, A. I. Cañzo, J. Org. Chem., 65, 2319 (2000).
- 15) T. Fedoroff, O. E. Sheffield, "Encyclopedia of explosives and related items", Vol. 1, p. A 42 (1960), Picatinny Arsenal.
- 16) A. Rieche: Ber. Dtsch. Chem. Ges., 75; 1016 (1942).
- 17) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", p. 250 (1992), John Wiley & Sons.
- 18) K. M. Mackay, R. A. Mackay, "Introduction to Modern Inorganic Chemistry", p. 93 (1989), Englewood Cliffs.
- 19) J. R. Bowser, "Inorganic chemistry", p. 312, 314-315 (1993), Wadsworth Inc.
- 20) D. F. Shriver, P. W. Atkins, C. H. Langford, "Inorganic chemistry", p. 150 (1990), Oxford University Press.