Thermal instability and kinetics analysis on triacetone triperoxide (TATP)

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Abstract. Differential Scanning Calorimetry (DSC), Thermogravimetry(TG) and vent sizing package 2 (VSP2) were performed to understand thermal behavior and decomposition kinetics of triacetone triperoxide (TATP) under non-isothermal and adiabatic conditions, respectively. Then the maximum self-heating rate \([dT/dt]_{\text{max}}\), maximum pressure rise rate \([dP/dt]_{\text{max}}\) were acquired. DSC studies revealed a coupling phenomenon of decomposition reaction and phase transition. Based on the DSC data, the thermal decomposition kinetic parameters were worked out and compared through the Friedman and ASTM E698 methods. The results indicated that Heat of decomposition (\(\Delta H_d\)) was extraordinary large even up to 2700 Jg⁻¹ for which recrystallized with methanol merely. The activation energy of which used methanol to recrystallize was 155.5kJ/mol by (ASTM) E-698 methods. By Friedman method Linear regression was able to reach a high enough level when the reaction progress (α) was between 0.1–0.9. The results can be used to calculate the optimal parameters for processing a safer design and establish the database of TATP for loss prevention protocol.

1. Introduction

Cyclic organic peroxides, triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane, TATP) is belonging to peroxide explosives (PEs) [1]. TATP is a whiteness, high explosives, insoluble in water, sourness granular solid and more than one unstabily peroxy bonds (O-O) (Fig.1). Thermal analysis study of energetic materials is essential for understanding the decomposition kinetics and assessing the potential hazardous in handing, processing and storage [2]. Recently, the thermal instability and decomposition of TATP was investigated for process safety by thermal analysis techniques. It can be synthetized with certain proportion of hydrogen peroxide (H₂O₂), acetone (CH₃COCH₃), and acid under low reaction temperature environment [3]. The oxidizability of hydrogen peroxide is very powerful that it is considered a high reactive oxygen species. Unlike most other explosives, TATP even can explode in wet or underwater. TATP exploded by rapidly decomposing each solid molecule into four gaseous molecules, and with no heat in the process of explosion. This rare phenomenon is scientifically called the "entropy explosion" [4]. It was well known in a serious explosion which happened in the subway in London, UK on July 07, 2005 [5]. A recent terrorist explosion was also shocking which happened on Nov. 13, 2015 in French and as the
Islamic State was building the machinery to mount sustained terrorist strikes in Europe. As a new type of energetic material, the dangerousness and stability are worth studying to TATP.

TATP has a large number of peroxide functionality, it is usually be added to organic media in the form of dilute solutions and as evocating agent in polymerization when using in the production of resin. TATP has been studied by scholars all along. Influence of reaction conditions (catalyst type, the catalyst to acetone ratio, and reaction temperature) on product composition was been studied by several authors and two products (TATP and diacetone diperoxide, DADP) by different ratio were compareative [6,7]. Furthermore, the differences in the vapor pressures of TATP synthesized without recrystallization was been investigated by thermogravimetric analysis (TGA) [8]. On the other hand, Wu S H explored two different acid catalysts (H2SO4; 98% w/v, HCl; 37% w/v) as catalyst by differential scanning calorimetry (DSC) and Gas chromatography/mass spectrometry (GC/MS) establishing thermal hazard and estimate the risk levels[9].

This paper aims to study the thermal performance and decomposition kinetics of TATP under different temperature programs by DSC, TG, and VSP2, respectively.

Fig.1. Optimized structure of TATP rock-steady structure

2. Experiments and method

2.1. Preparation

TATP was prepared following the way described in literature by mixing chemicals (Table 1) under the right conditions could get rough product [10]. Handlers should be careful about the temperature control, ratio of each reagent, and reaction time during collocation because about two grams of TATP can explode under open conditions. Then, the mixture would react at room temperature for about 12 hours. Finally, the mixture would be washed to neutral with distilled water and get crude product (TATPc) after filtration and drying. The last step is recrystallized of TATPc by methanol.

Table 1. Parameters of reagents required for the formulation of TATP.

| Name                | Abbreviation | Mass Fraction/wt–% | CAS number   |
|---------------------|--------------|--------------------|--------------|
| hydrogen peroxide   | H2O2         | 30                 | 7722-84-1    |
| acetone             | CH3COCH3     | –                  | 67-64-1      |
| hydrochloric acid   | HCl          | 37                 | 7647-01-0    |
2.2. Examination of the molecule
Prior to undertaking any experimental studies on an energetic material, the examination of the molecule for energetic functional groups should be the starting point for any such evaluation [11]. Density functional theory (DFT) at B3LYP/6-311+G (d, p) level was used to analyze the bond dissociation energy (BDE) of TATP. The calculation results in GAUSSIAN indicated that the -o-o- atom with a low BDE can be easily ruptured and thus result in the instability of TATP.

2.3. Thermal studies under non-isothermal conditions by DSC and TG
PerkinElmer Pyris 1 TG was used to perform decomposition experiments. The heating rate was set at 2 °C min⁻¹, and the heating range was between 30 and 300 °C. The experimental gas of TG was purity nitrogen, and the flow rate was 20 mL min⁻¹.

The thermal analysis tests were carried out by a Mettler Toledo DSC-821. As the common instrument of conventional thermoanalysis, DSC is fast and easy to operate. Through DSC tests, we could get temperature-heat flow curves, and the various thermokinetic parameters were obtained by Thermal Analysis System Software. DSC was performed the heating rates at 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹ and the test temperature range was set at 30-250 °C in this study. The selected temperature range was determined by a thermal cracking test from thermogravimetry (TG) which has the ability to investigate the thermal cracking of materials of interest.

2.4. Vent sizing package 2 (VSP2)
VSP2, a PC–controlled adiabatic calorimeter, is produced by Fauske Associates, Inc. [12]. It could obtain thermal kinetic parameters and thermal hazard parameters. \( T_o \) in DSC was read as setting begin of wait-temperature. The samples was put in small glass container and then place in the test cell (ca. 112ml) [13], then continue to heat 10 degrees after waiting for ten minutes.

3. Results and discussion
3.1. Thermal behavior of TATP under non-isothermal conditions
Fig.2 TG and DTG curves at different heating rates under nitrogen atmosphere. It shows the mass loss and mass loss derivative curves of TATP at heating rate of 0.5, 1.0, 2.0, 4.0, and 8.0 °C min⁻¹ in a dynamic atmosphere of nitrogen. From the TG curves, it can be seen one stage of mass loss and the decomposition was quickly, probably due to the volatility of TATP.

DSC studies were then carried out as a supplement to TG data. Figure 3 showed a melting process and two decomposition processes. Particularly, the latter decomposition process was weak and hard to observed in DSC curves, and the endothermic peak was followed by the exothermic peaks, which was defined as “a coupling phenomenon of heat absorption and generation” [11]. The characteristic parameters of DSC tests such as onset temperature \( (T_o) \), peak temperature \( (T_p) \) and decomposition heat
(\(\Delta H_d\)) were shown in Table 2. It can be found that the reaction released less energy at higher heating rate.

![Fig. 3. Non-isothermal DSC curves of TATP under various heating rates.](image)

**Table 2. Thermal characteristic parameters of TATP obtained by DSC.**

| \(\beta\) (°C min\(^{-1}\)) | Msss (mg) | \(T_0\) (°C) | \(T_{\text{max}}\) (°C) | \(\Delta H_d\) (Jg\(^{-1}\)) | Peak Height/mw |
|-----------------------------|----------|--------------|----------------|----------------|----------------|
| 0.5                         | 3.05     | 184.85      | 187.02        | 2895.79        | 27.28          |
| 1.0                         | 3.18     | 195.39      | 203.28        | 2468.67        | 11.82          |
| 2.0                         | 3.08     | 204.18      | 206.97        | 2763.60        | 26.27          |
| 4.0                         | 3.12     | 170.17      | 210.73        | 2327.25        | 13.01          |
| 8.0                         | 3.03     | 176.13      | 218.73        | 2453.79        | 23.06          |

TATP at 0.5, 1.0, 2.0, 4.0 and 8.0 °C min\(^{-1}\) and engendering a different exothermic reaction after heating in 30 to 250 °C temperature range. The peak of the reaction is clear and simple again to prove the purity of the configuration samples. As samples are solid, it was inevitable that there is a phase transition process in the procedure of heating up. The amplified part of the picture is the endothermic peak. The heat flow values of decomposing reaction were all higher than 2000 J/g. It was greater than the defined heat flow value which was 1000 J/g [14]. It is very dangerous, and it fits as an energetic material.

### 3.2. Calculation of thermokinetic parameter

In general, the combustion characteristics of TATP is flammable, so we must pay more attention to the hazardous information. Therefore, we hope the kinetic models can help us to establish the mechanism of preventing disaster of TATP. According to the test methods from the American Society for Testing and Materials (ASTM) E-698 and Friedman which can evaluate \(E_a\) by thermokinetic model. Throughout the course of the reaction, the activation energy (\(E\)) and the pre-exponential factor (\(A\)) were function of \(\alpha\):

\[
\beta \frac{d\alpha}{dT} = A(\alpha) \exp \left( -\frac{E(\alpha)}{RT} \right) f(\alpha)
\]

Differential equation gotten from two side logarithm obtained:

\[
\ln \left( \beta \frac{d\alpha}{dT} \right) = \ln \left( A(\alpha) \right) - \frac{E(\alpha)}{RT}
\]
The formula is displayed to ASTM E698:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) e^{-E(\alpha)/RT} f'\left(\alpha\right)$$  \hspace{1cm} (3)$$

Where $\alpha$ is fractional reaction; $t$ is time (s); $A(\alpha)$ is pre-exponential factor (s$^{-1}$); $f(\alpha)$ is a differential reaction model; $E$ is activation energy (J/mol); $T$ is absolute temperature (K); and $R$ is the general gas constant (J/mol K).

According to Fig. 4, it could be apparent activation energy of TATP by Friedman method. The differential method Friedman was not involved in any assumptions or approximation on the basis of formula (2). The result of this calculation was more accurate and approximated to the truth. It was not a stable value and could conjecture that they were a multistep reaction in the non-isothermal decomposition process. Linear regression was able to reach a high enough level when the reaction progress ($\alpha$) was between 0.1–0.9. Therefore, it was reasonable in the range of data points. Through the Friedman equal conversion method getting the $E_a$ and $\ln(A(\alpha)f(\alpha))$ were within a reasonable range. According to the test methods from the American Society for Testing and Materials (ASTM) E-698. The result of the calculation is 155.5 kJ/mol.

![Fig. 4. Activation energy of TATP by Friedman method.](image)

### 3.3. Data evaluations by VSP2

TATP was evaluated by VSP2, and the experimental phenomena were shown as illustrated in Fig. 5. In the process of experiment, the glassware with TATP in virtue of the self-heating temperature reached, sample exploded and release heat and pressure. It was able to read the change of temperature and pressure clearly. We could clearly see TATP power and did not do it over and over again. Table 3 lists some experimental parameters of VSP2 including $T_0$ (°C), $T_{max}$ (°C), $P_{max}$ (bar), $(dT/dt)_{max}$ (°C min$^{-1}$), and $(dP/dt)_{max}$ (bar min$^{-1}$).

![Fig. 5. The glassware to TATP for the beginning and end the VSP2 tests.](image)
Fig. 6. Temperature and pressure vs. time curves for TATP by VSP2 tests.

Table 3. Thermal hazard date of TATP<sup>0</sup> and TATP<sup>3</sup> by VSP2 test.

| Sample | T<sub>0</sub> (°C) | T<sub>max</sub> (°C) | P<sub>max</sub> (bar) | (dT dt<sup>-1</sup>)<sub>max</sub> (°C min<sup>-1</sup>) | (dT dt<sup>-1</sup>)<sub>max</sub> (bar min<sup>-1</sup>) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TATP   | 151.4           | 279.6           | 123.9           | 12077.9         | 19022.9         |

4. Conclusions
The thermal behavior and decomposition kinetic of TATP under non-isothermal and adiabatic conditions were studied by DSC/TG and VSP2 respectively. There was one main mass-loss stages in TG curve, and the DSC curve showed that the endothermic peak was followed by the exothermic peaks. <i>E_a</i> dependency was evaluated by (ASTM) E-698 method.

So we need pay attention for this work. TATP is suitable as a new type of energetic material, because it has enormous energy and product cleanliness.

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References
[1] McDonnell G, Russell A D. Clin Microbiol Rev. 12, 147 (1999).
[2] JQ Zhang, HX Gao, TZ Ji, KZ Xu, RZ Hu. J Hazard Mater. 193, 183 (2011).
[3] Dunayevskiy I., Tsekoun A., Prasanna M., Go R., Patel C. K. N. Appl. Opt. 46, 6397 (2007).
[4] Malashikhin S, Finney N S. J Am Chem Soc. 130, 12846 (2008).
[5] Cotte-Rodríguez I, Chen H, Cooks R G. ChemComm. 9, 953 (2006).
[6] Oxley J C, Smith J L, Bowden P R, Rettinger R C. Propellants Expl. Pyrotech. 38, 244 (2013).
[7] Oxley J C, Smith J L, Steinkamp L, Zhang G. Propellants Expl. Pyrotech. 38, 841 (2013).
[8] Mbah J, Knott D, Steward S. Talanta. 129, 586 (2014).
[9] Wu S H, Chi J H, Wu Y T, Huang Y H, Chu F J, Homg J J, Shu C M, Charpentier J C. J Loss Prev Proc Ind. 25, 1074 (2012).
[10] Milas N A, Golubović A. J Am Chem Soc. 81, 1745 (1959).
[11] Rowe S M. Process Res Dev. 6, 877 (2002).
[12] Manual V S P. Methodology; Fauske & Associates. Inc.: Burr Ridge, IL, (1996).
[13] Liu S H, Shu C M. J Therm Anal Calorim. 121, 533 (2015).
[14] Heemskerk A H, Hordijk A C, Lanning A T, Lont J C, Schell H, Schuurman P. AIChE Center for Chemical Process Safety: New York, (1995).