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Thermokinetic Investigation of o-Nitrotoluene Using Reaction Calorimetry

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ABSTRACT:

O-nitrotoluene (2-NT) is an important chemical widely used in the chemical industry. However, in the past 25 years, severe incidents have killed 10 people and injured more than 200 due to its thermal decomposition. This research focus on the thermal behavior of 2-NT decomposition. Advance Reactive System Screening Tool (ARSST) and the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) have been used to better understand the mechanisms that result in the explosion hazard of 2-NT. Key parameters such as observed onset temperature, onset pressure, self-heat rate, and pressure rate have been reported. Furthermore, the APTAC data is used in the calculation of Arrhenius data, reaction order, and self accelerating decomposition temperature (SADT). The results show that the 2-NT decomposition reaction has potentially severe consequences and is sensitive to the conditions like sample size and initial pressure. Also, there are two peaks in self-heat rate profile in the ARSST tests which indicate a minimum two different reactions that may be occurring during the decomposition. This study also focuses on the kinetics of the decomposition reaction which is nearly zero-order reaction and SADT prediction of the 2-NT of UN 25 kg package storage.

Key words: o-nitrotoluene (2-nitrotoluene), thermal decomposition, ARSST, APTAC, adiabatic calorimeter, reaction order, SADT

1. Introduction

O-nitrotoluene (2-NT) is listed as a high production volume chemical according to U.S. Environmental Protection Agency (EPA), with the production of 2-NT in the USA between 1986 – 2002 reaching between 10 million and 50 million pounds [4.5 million and 22.7 million tonnes] [1]. According to 2010 data, 2-NT is produced by 10 companies in the U.S., seven companies in the People's Republic of China, three companies in the United Kingdom, two companies in Canada, and one company each in the Czech Republic, Germany, India, Italy, Japan and Switzerland [2]. Except for producing the dinitrotoluenes, pure 2-NT can also be consumed in smaller specialty markets, like the production of dyes, rubber chemicals, and agricultural chemicals [3]. 2-NT is a combustible chemical but takes some effort to ignite [4]. 2-NT will decompose under certain conditions which include elevated temperature, presence of impurities, and being held at more moderate temperatures for an extended time. Historically, incidents have happened involving the thermal decomposition of 2-nitrotoluene which caused fatalities and injuries as shown in Table 1.

Table 1

Incidents of fires or explosions caused by o-nitrotoluene [5,6,7]

Date	Location	Company	Injuries	Fatalities	Hazard	Cause
05/11/2007	Cangzhou, China	China National Chemical Corporation	80	5	Explosion (reactor)	Incompatible contamination
10/13/2002	Pascagoula, Mississippi	First Chemical Corporation	3	0	Explosion (distillatory)	Thermal decomposition
09/21/1992	United Kingdom	Hickson & Welch Ltd	181	5	Explosion (distillatory)	Thermal decomposition
08/07/1972	Institute, West Virginia	Union Carbide Facility	1	0	Explosion (pipeline)	External heat

Thermal decomposition of 2-NT has been studied in literature using different calorimetries. Ando et al. [8] used several milligrams of 2-NT at 3.5 MPa in a Differential Scanning Calorimetry (DSC) and reported an observed onset temperature of decomposition of 338 °C and a heat of decomposition of 1.32 kJ/g. Similar DSC tests done by Duh et al. [9] found an observed onset temperature of 290 °C and a heat of decomposition of 2.40 kJ/g. Accelerating Rate Calorimetry (ARC) tests of 2-NT were studied by Shachdev et al. [10] and a heat of reaction of 131 kJ/g with the observed onset temperature of 250 °C. 2-NT may decompose explosively if heated above 190°C [11]. Bateman et al. [12] performed isothermal exposure tests at temperatures between 150 and 230 °C in a closed vessel. The isothermal induction period for the production of decomposition gas was found to be 31 days at 150 °C. The decomposition of 2-NT is rapid and highly exothermic. This is due to the following factors:

- (1) The decomposition occurs at higher temperatures (250-350 °C), where the activation energy is higher and endothermic reactions more likely to happen.
- (2) The heat of decomposition is very high (>1300 J/g). Consequently, under pseudo adiabatic conditions or at normal process conditions, the decomposition reaction rate will accelerate due to a fast increase of the temperature.

The decomposition mechanisms for nitro aromatic compounds are very complex. For 2-NT, there are 3 different initial pathways that can occur. The primary decomposition pathways are shown in Fig 1. C-NO₂ homolysis is a dominant decomposition pathway of 3- and 4- nitrotoluene, and also occurs for 2-nitrotoluene [13,14,15,16]. Evidence of the nitro-nitrite rearrangement of 2-NT exists primarily in the gas phase and in a dilute solution. In the condensed phase, the evidence is more circumstantial [17]. Several studies prove the C-H alpha attack is a primary decomposition pathway for TNT, 2,4-DNT, and o-MNT [18,19,20]. Summary of the kinetic data for each step is summarized in Table 2.

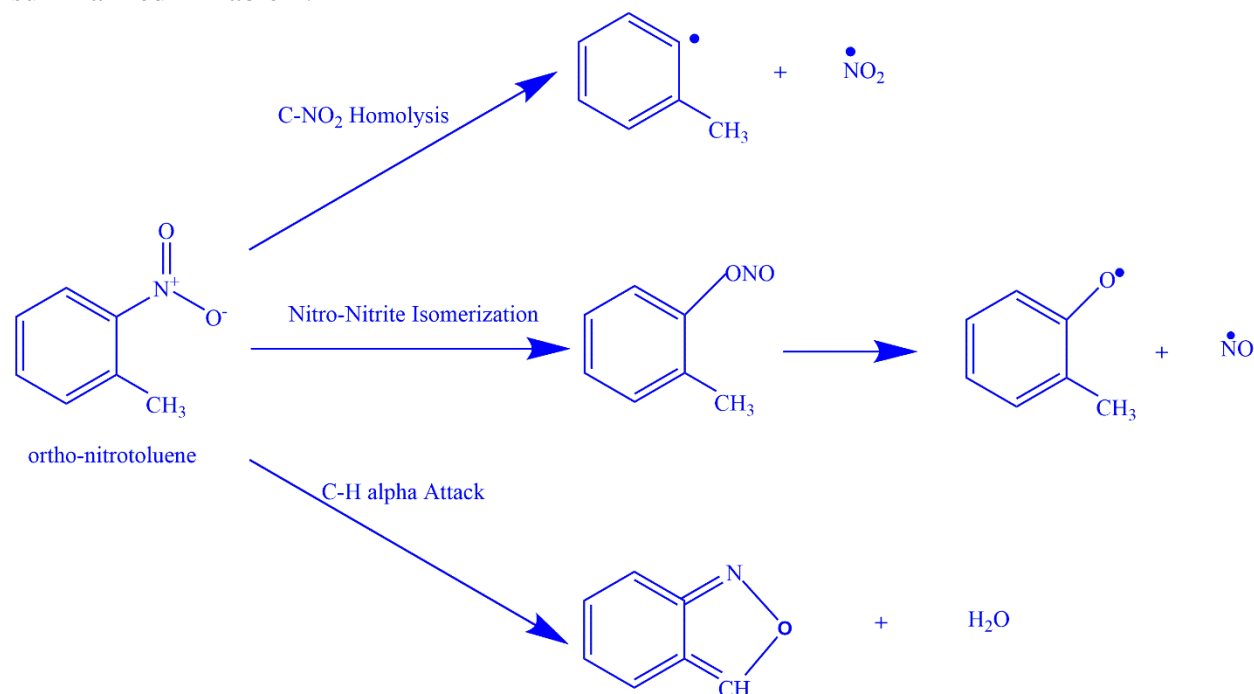


Fig 1. Decomposition pathways of the o-nitrotoluene.

Table 2

Arrhenius Data for Decomposition of 2-NT

Pathway Type	T, [°C]	E _a , [kJ/mol]	A, [s ⁻¹]	Ref.
C-NO ₂ Homolysis	797-907	257.19	10 ^{14.84}	[15]
	827-977	280.33 ± 9	10 ^{16.4±0.8}	[14]
C-H alpha Attack	300-350	177.82	10 ^{10.22}	[17]
	400-450	207.11±5	10 ^{12.4±0.4}	[16]
	797-907	215.60	10 ^{13.08}	[15]

However, incidents still keep happening which indicates more studies should be done to fully understand the thermal behavior of 2-NT. In this study, thermal decomposition of pure liquid 2-NT has been studied using an Advanced Reactive System Screening Tool (ARSST) and Automatic Pressure Tracking Adiabatic Calorimeter (APTAC). This paper is the first one to report the decomposition data of 2-NT using the ARSST and APTAC. Parameters important in the characterize action of the thermal behavior of 2-NT, include the observed ‘onset’ temperature (T_{onset}), ‘onset’ pressure (P_{onset}), maximum self-heat rate ([dT/dt]_{max}), maximum pressure rate

($[dP/dt]_{\max}$), and maximum temperature (T_f) are studied. The results provide thermal hazard information about 2-NT for process industries helping establish effective emergency programs. Other important parameters presented in this work include self-accelerating decomposition temperature (SADT) and temperature of no return (T_{NR}) which used to predict vessel temperature for transportation and storage.

2. Experimental

2.1 Sample

2-Nitrotoluene (Aldrich, $\geq 99\%$, ACS Reagent) was used without further purification

2.2 Advanced Reactive System Screening Tool (ARSST)

The ARSST is a pseudo adiabatic calorimeter manufactured by Fauske. It consists of three major parts: the containment vessel, control box, and computer. The standard containment vessel (volume 350 cm^3) holds an open test cell (typically 10 cm^3), thermocouples, and an insulation assembly around the test cell. The containment vessel is attached to a pressure transducer to measure the pressure inside the containment vessel. Temperature measurement ranges from $-50 \text{ }^\circ\text{C}$ to $700 \text{ }^\circ\text{C}$ and the pressure measurement range is from 0 to 500 psig for the standard vessel with a rupture disk set at 900 psig. There are seven different control modes for the ARSST [21] and the single ramp-polynomial control is the most commonly used method. This method can provide a constant power to the sample over a specific temperature range and the sample could be heated up smoothly compared to the other methods. Therefore, in this study we also used the single ramp-polynomial control. In a typical experiment, liquid 2-NT (0.5 ml to 2 ml) is weighted and then injected into the 10 ml test cell using pipette.

2.3 Automatic Pressure Tracking Adiabatic Calorimeter (APTAC)

APTAC is a very powerful tool to assess the thermal hazards of reactive chemicals. The APTAC is an adiabatic calorimeter which minimizes heat losses by maintaining the sample temperature surroundings external to the test cell very close to the temperature of the sample. Also, the pressure compensation mechanism automatically adjusts the pressure outside of the test cell to equal the pressure inside the test cell, allowing the equipment to perform high pressure tests. The temperature range is from ambient to $500 \text{ }^\circ\text{C}$ and the pressure rang from vacuum to 2000 psig. Regarding the temperature control during the tests, heat-wait-search mode was used: the sample was heated at $10 \text{ }^\circ\text{C}/\text{min}$ to a starting temperature, and the temperature was allowed to stabilize for 30 min, following which the APTAC searched for exothermic behavior. If the self-heat rate of the sample was greater than a preset threshold ($0.05 \text{ }^\circ\text{C}/\text{min}$), the equipment tracked the reaction adiabatically until the reaction ended or one of the shutdown criteria was met. In a typical experiment, liquid 2-NT is weighted and then loaded into a test cell which can vary from 0.5 ml to 2 ml.

3. Results and Discussion

3.1 ARSST Tests

In this section, the experimental thermal decomposition of pure 2-NT under various different conditions are described. The temperature, self-heat rate, pressure and pressure rate are shown in Fig. 2 for three duplicate tests. When the temperature reaches $300 \text{ }^\circ\text{C}$ which is the onset temperature, both the temperature and pressure will increase dramatically. It is most obvious when

looking at the self-heat rate and pressure rate shown in Fig. 2 (c) and (d). The pressure rate data for ARSST tests has been treated by using the Savitzky-Golay method with a 5-point window. In this study, the onset temperature is defined from the self-heat rate profile. A tangent is drawn to the curve where the self-heat rate starts to increase, then a straight line is drawn on the end of the self-heat rate curve before the temperature starts to increase rapidly. For 2-NT, the observed onset temperature was determined to be 310 (± 10 °C) from the three duplicated tests. The T_{max} is defined as the temperature when the maximum self-heat rate occurs. T_f is the temperature when the reaction completes or the self-heat rate equals to zero. From Fig 2., the maximum self-heat rate is as high as 282 °C/s and the maximum pressure rate is 969 psig/s for the 350 cm³ containment vessel. T_{max} is 455 °C and T_f could be as high as 617 °C. However, the max values are still conservative since they happened after the shut-down criteria of the experiment was reached (450 °C). After 450 °C, the heater will stop heating the sample and the heat loss to the environment will be significant. More details of each experiment are listed in the Table 3.

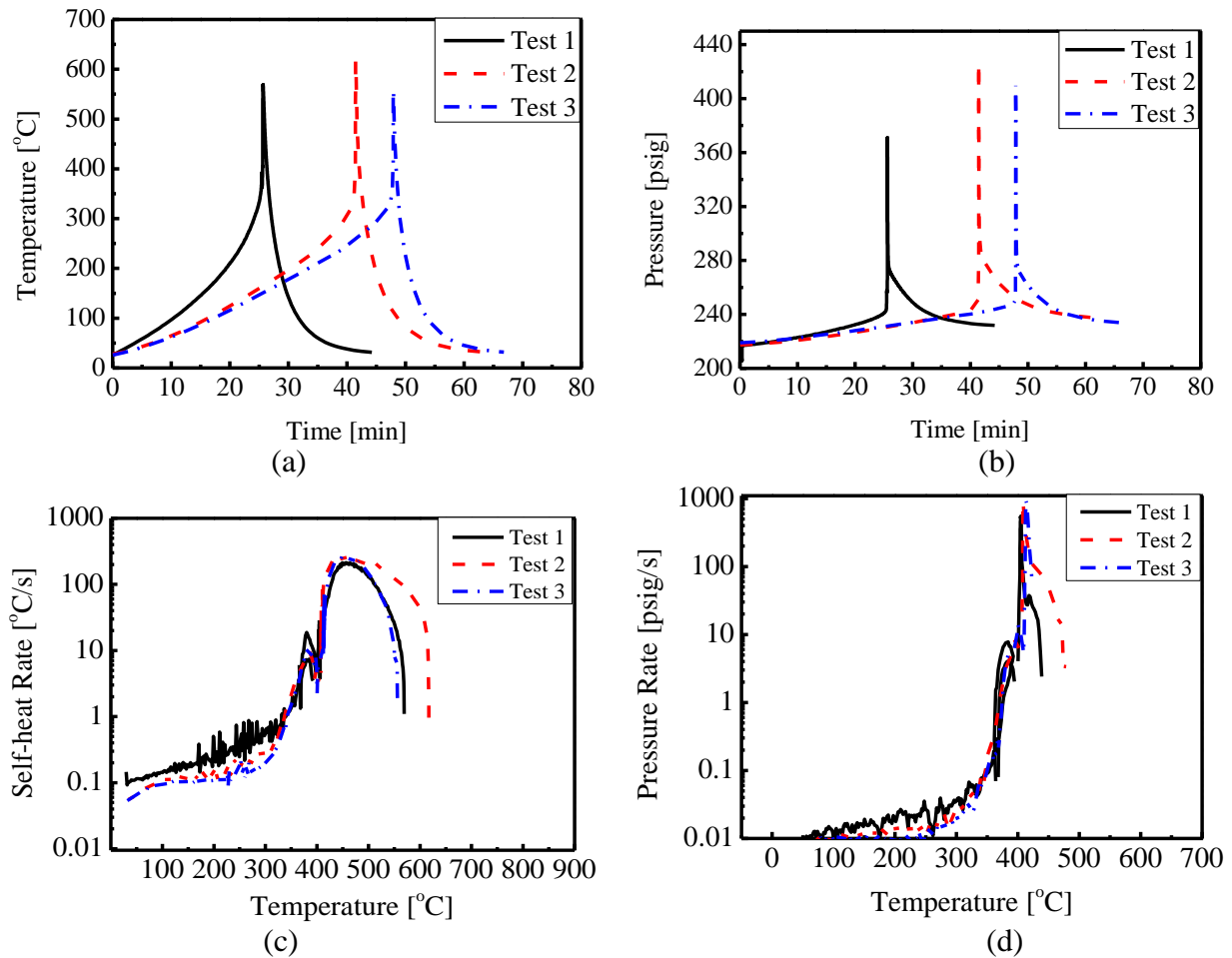


Fig 2. The thermal decomposition of 2-NT (a) Temperature profile (b) Pressure profile (c) Self-heat rate (d) Pressure rate

In this study, the thermal inertia factor, \emptyset is calculated using Equation (1) and the result is near 1.20.

$$\emptyset = \frac{m_s c_{p,s} + m_c c_{p,c}}{m_s c_{p,s}} \quad (1)$$

where m is mass, and C_p is the heat capacity. The subscript s and c respectively stand for the sample and the cell (glass).

If it is assumed that the heat capacity C_p is not the function of temperature, then the heat of reaction $-\Delta H_{rxn}$ can be calculated by Equation (2). [22]

$$\Delta H_{rxn} = \frac{-m \cdot \phi \cdot C_p \cdot (\Delta T_{ad})}{n_{rxn}} \quad (2)$$

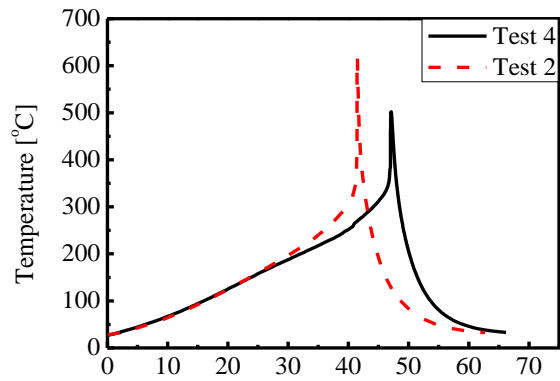
In this equation, m is the sample mass, ϕ is the thermal inertia factor from Eqn. (1), C_p is the heat capacity of the sample mass, and n_{rxn} is the moles of 2-NT reacted. ΔT_{ad} represents the adiabatic temperature raise, which is the difference between the final and initial temperatures over the course of an exothermic period. For the ARSST, $\Delta T_{ad} = T_f - T_o - \Delta T_{external}$. $\Delta T_{external}$ stands for the ARSST input power. The heat capacity used for 2-NT is $1.47 \text{ J g}^{-1} \text{ K}^{-1}$ [23]. T_o is the observed onset temperature which is listed on Table 3.

Table 3 Pure 2-NT ARSST experimental data

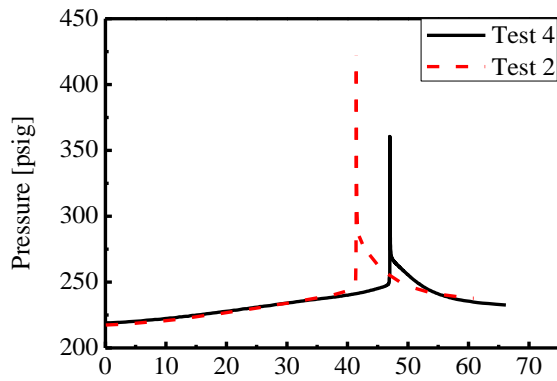
Test no.	Sample Size	Initial P [psig]	T_{onset} [°C]	P_{onset} [psig]	$(dT/dt)_{max}$ [°C s ⁻¹]	$(dP/dt)_{max}$ [psig s ⁻¹]	T_{max} [°C]	T_f [°C]	P_{max} [psig]	$-\Delta H_{rxn}$ [kJ mol ⁻¹]	Phi (ϕ)
1	2.36	220	310	226.6	213	600	455	569	356	70	1.34
2	2.37	220	315	248	282	969	455	617	426	83	1.37
3	2.36	220	304	249	263	968	457	556	410	68	1.35
4	1.20	220	326	257	148	733	423	502	361	58	1.64
5	2.32	126	346	146	53	5.82	443	463	161	55	1.37

Tests of two different sample sizes are shown in Fig. 3. Test 2 has approximately 2 times the amount of 2-NT as compared to Test 4 at 2.37 g and 1.20 g respectively. The results show larger sample sizes lower the observed onset temperature which makes large scale tests important. Due to the higher thermal inertia and smaller sample size, test 4 has smaller $(dT/dt)_{max}$ and $(dP/dt)_{max}$. Tests of two different initial pressure are shown in Fig. 4. Test 5 and Test 1 have similar sample quantity. However, test 5 is conducted with a lower initial pressure (126 psig) compare to test 1 (220 psig). Lower initial pressure increases the onset temperature, and lowers the self-heat rate. ARSST tests are open cell, thus sample phase shift from liquid to vapor will occur during heat up. This latent heat will lower the observed onset temperature.

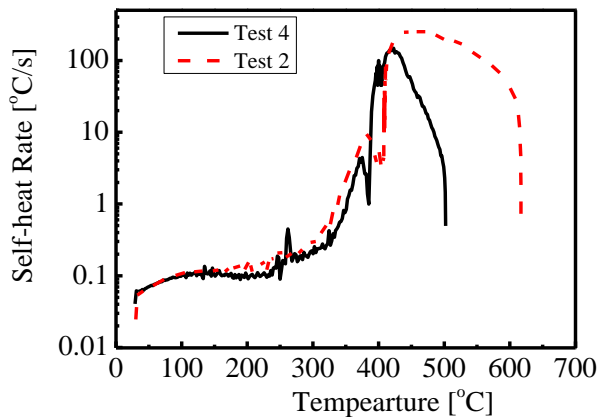
For the ARSST results shown here, there are two peaks in the self-heat rate graphs. This is likely due to distinct reactions happening during the thermal decomposition process. The first reaction happens at a lower temperature and releases less heat while the second reaction happens at a higher temperature but release much more heat. The first reaction might be the C-H alpha attack and the second reaction maybe the combination of C-NO₂ homolysis and nitro-nitrite rearrangement.



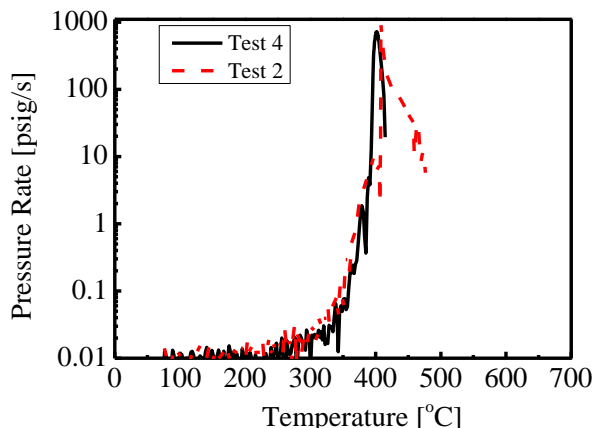
(a)



(b)

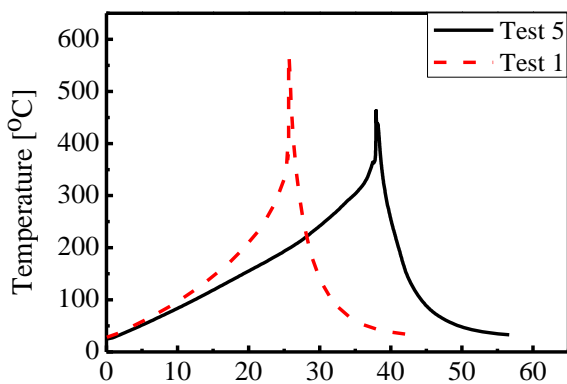


(c)

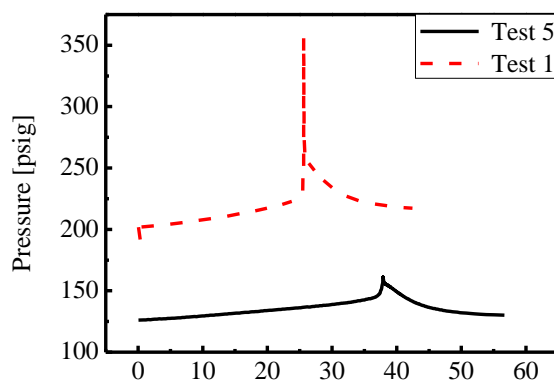


(d)

Fig. 3 The thermal decomposition of two different sample sizes of 2-NT (a) Temperature profile (b) Pressure profile (c) Self-heat rate (d) Pressure rate



(a)



(b)

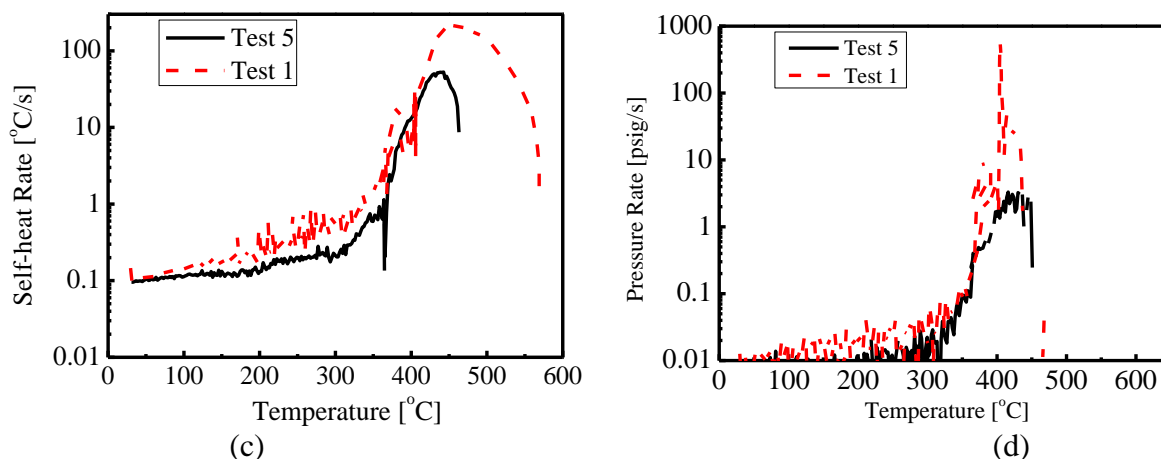


Fig. 4 The thermal decomposition of two different initial pressure of 2-NT (a) Temperature profile (b) Pressure profile (c) Self-heat rate (d) Pressure rate

3.2 APTAC Tests and Kinetics

In this section, the kinetics of the 2-NT decomposition reaction is determined using the APTAC results. Experimental details of the two tests used in this section are listed in Table 4. The temperature profile for Test A and Test B with heat-wait-search mode are shown in Fig. 5. Data of when the decomposition reaction starts to the end of adiabatic condition is used in the calculation of the thermokinetics of the decomposition and also the corresponding temperature profile, self-heat rate, pressure profile and pressure rate are drawn in Fig 6 (Test A) and Fig 7. (Test B). For Test A which has 2.34 gram of 2-NT, the onset temperature starts from 279 °C, the maximum self-heat rate is 6889 °C/min and the maximum pressure rate is 1619 psig/min in the 100 cm³ test cell. The heat of the reaction is 462 kJ/mol which is larger than the ARSST results (83 kJ/mol). Test A has approximately 1.3 times the amount of 2-NT as compared to Test B at 2.34 g and 1.77 g respectively. The results show larger sample sizes lower the observed onset temperature. Also, the thermal inertia factor (Φ) can influence the maximum self-heat rate, pressure rate which make the low thermal inertia calorimeter tests important. Due to the safety considerations for Test B, when the temperature reaches 420 °C, the equipment will shutdown stopping heating of the system. Therefore, the calculated heat of reaction for Test B is much smaller than Test A. The expected value of Test B should be similar to Test A results which is around 500 kJ mol⁻¹.

Table 4

Pure 2-NT APTAC experimental data

Test No.	Sample Mass [g]	Mass of the cell [g]	P _{initial} [psig]	T _{onset} [°C]	P _{onset} [psig]	(dT/dt) _{max} [°C min ⁻¹]	(dP/dt) _{max} [psig min ⁻¹]	-ΔH _{rxn} [kJ mol ⁻¹]	Phi (Ø)
Test A	2.34	59.42	160	279	329	6889	1619	462	15.5
Test B	1.77	51.63	160	282	342	653	14	131	17.6

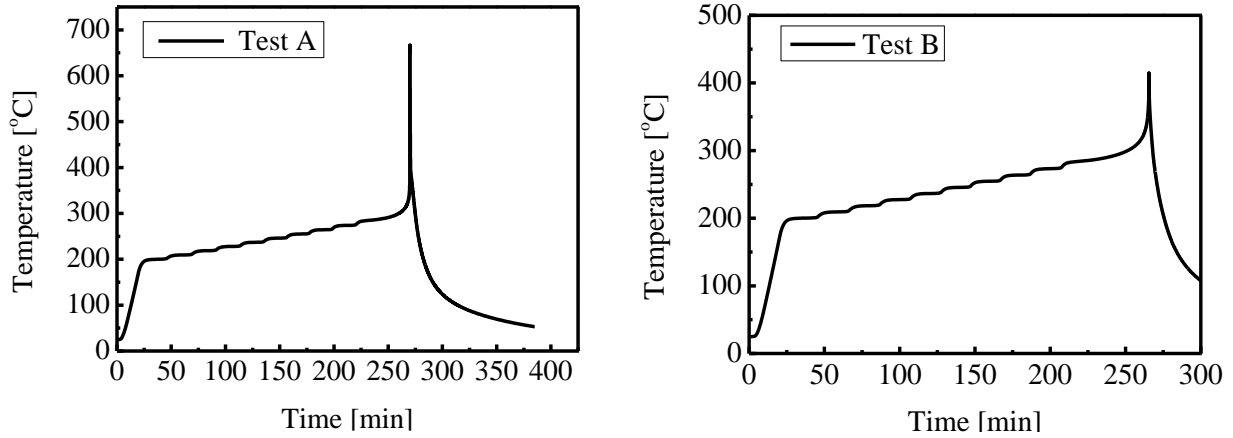


Fig. 5 Temperature profile of 2-NT decomposition in APTAC using Heat-wait-search mode

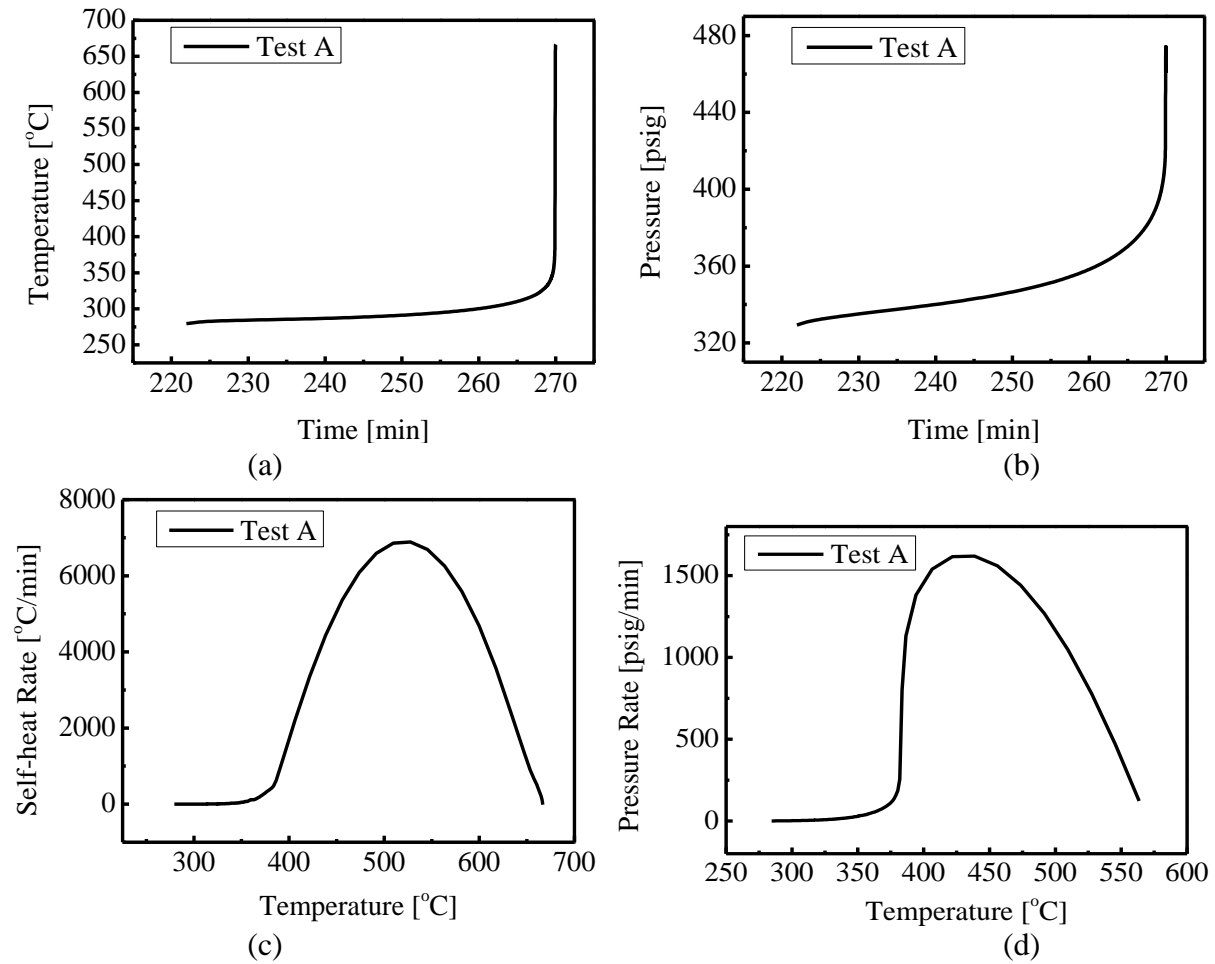


Fig. 6 Adiabatic decomposition reaction process of 2-NT in APTAC (Test A) (a) Temperature profile (b) Pressure profile (c) Self-heat rate (d) Pressure rate

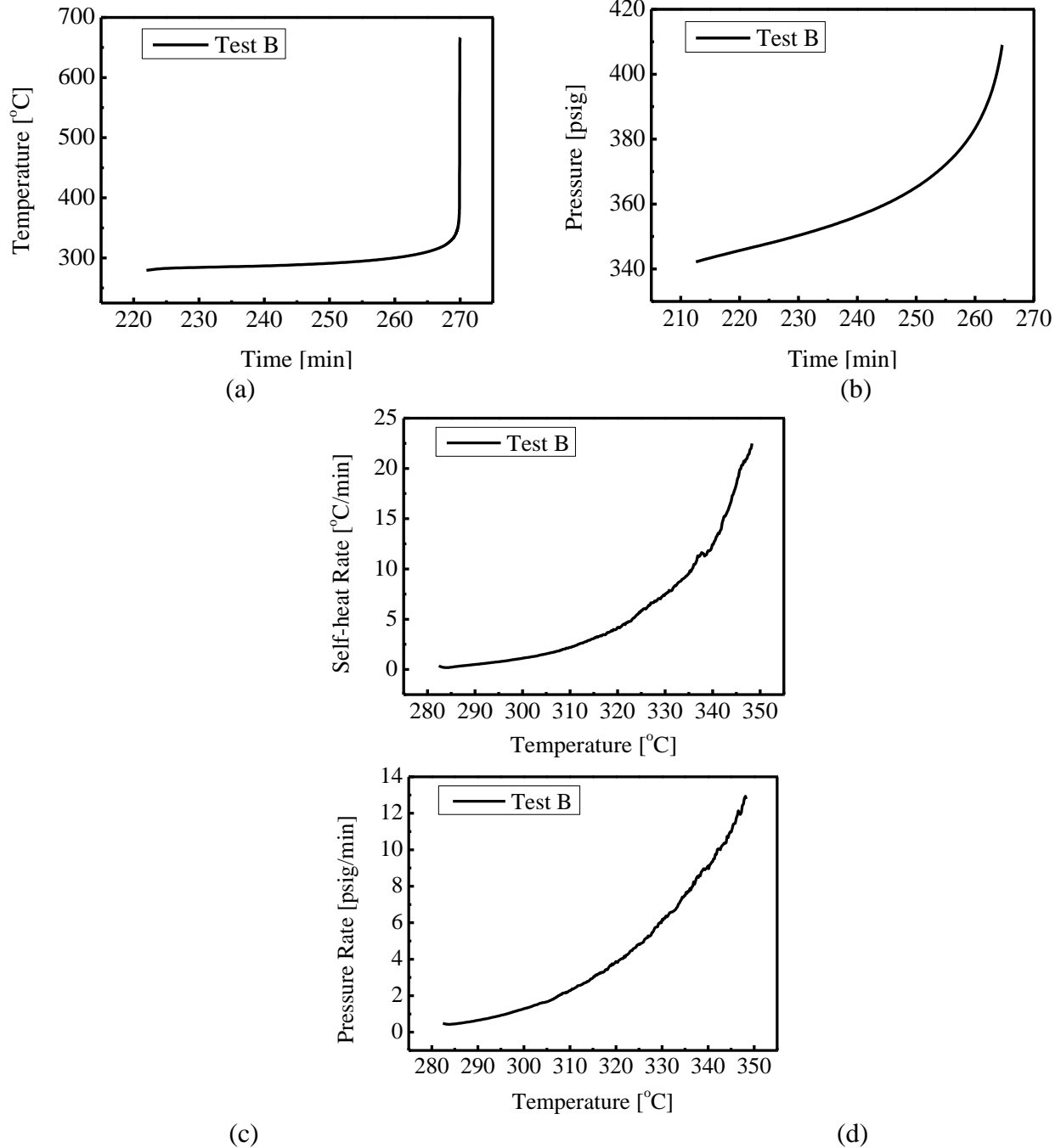


Fig. 7 Adiabatic decomposition reaction process of 2-NT in APTAC (Test B) (a) Temperature profile (b) Pressure profile (c) Self-heat rate (d) Pressure rate

When adiabatic, all the heat generated by the decomposition reaction will be used in the heating up of the sample and test cell, therefore, the energy balance equation is:

$$M\bar{c}_V \frac{dT}{dt} = M\Delta H_{r \times n} \frac{d(1-x)}{dt} \quad (3)$$

In this equation, \bar{c}_V is the average heat capacity of the system [J/(kg·K)], $\Delta H_{r \times n}$ is the heat of the reaction per mole reacted [J/g], x is the conversion fraction, range from 0 to 1.

From Equation (3), the adiabatic temperature increase ΔT_{ad} is expressed as

$$\Delta T_{ad} = T_f - T_0 = \frac{(-\Delta H_{rxn})}{c_v} \quad (4)$$

In this equation, T_f is the max temperature of the adiabatic reaction, T_0 is the onset temperature of the adiabatic reaction.

Equation (3) could also give us the relation between the conversion fraction x and temperature change:

$$x = \frac{T - T_0}{\Delta T_{ad}} \quad (5)$$

Then the temperature increase rate m_T of the adiabatic system is:

$$m_T = \frac{dT}{dt} = k \Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n = A \exp\left(-\frac{E_a}{RT}\right) \Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n \quad (6)$$

From Equation (6):

$$\ln \frac{m_T}{\Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n} = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (7)$$

Let $k = \frac{m_T}{\Delta T_{ad} \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n}$ then:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad (8)$$

According to Equation (8), given an appropriate value of n , then the relation between rate constant k and $1/T$ is linear. Then the intercept of the graph is the value of $\ln A$ and the slope equals to $-E_a/R$. Matlab nonlinear least-squares (`lsqnonlin`) function was used to get the A , K and n for Test A and Test B separately. The results are summarized in Table 5 and the correlation of overall rate constant (k) and temperature (T) shown in Fig. 7. The correlation coefficient for both fittings are nearly 1 which means the simulated results match very well with the experimental data.

Arrhenius Equation for the decomposition of 2-NT as found from the experimental results of this work is:

$$\mathbf{k=1.0e+14 \exp (-1.930e+05/(R*T)), R=8.314 \text{ J mol}^{-1}\text{K}^{-1}.$$

The reaction order n is 0.1, and we could treat the decomposition of 2-NT as zero-order reaction.

Table 5
Kinetic Parameters of 2-NT decomposition

Parameters	Test A	Test B
Rate Coefficient (A)	1.000e+14 s ⁻¹	1.000e+14 s ⁻¹
Activation Energy (E _a)	1.936e+05 J/mol	1.924e+05 J/mol
Reaction Order (n)	0.1	0.1
R ²	0.99515	0.99218

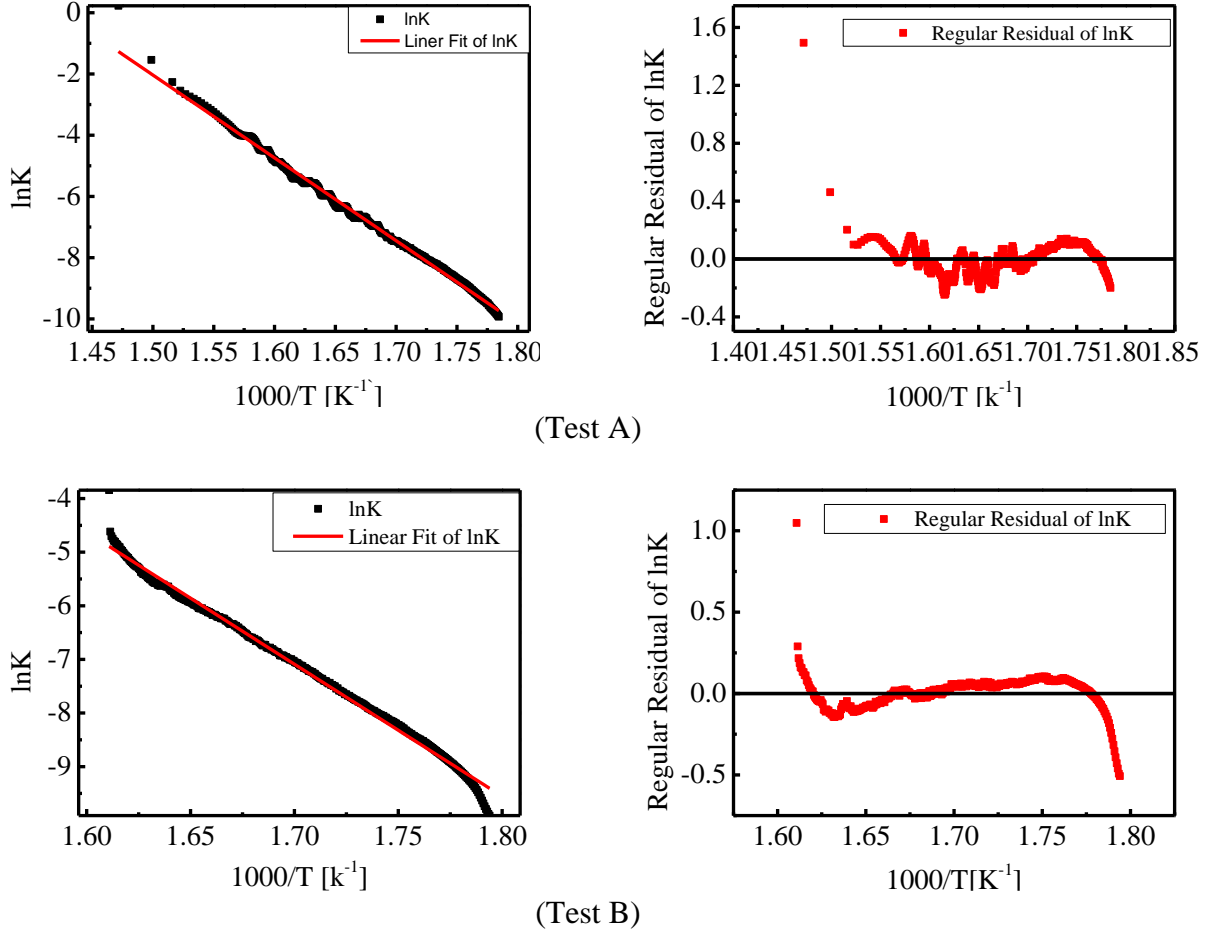


Fig. 8. The correlation of overall rate constant (k) and temperature (T) for Test A and Test B and the corresponding residual of lnK

3.3 SADT Calculation

The heat generation rate by the decomposition of reaction of the 2-NT is,

$$q_G = \frac{dH}{dt} = \Delta H_{rxn} M^n A \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

Where q_G is the heat generation rate; n is the reaction order; M is the mass of reactant, g; E_a is the activation energy, J/mol; A is pre-exponential factor, s^{-1} ; R is the universal gas constant, J/(mol·K). Referring to the Semenov model [24] which assumes uniform temperature distribution and the heat release to the environment all happens on the surface, then the heat release rate to the environment is

$$q_L = US(T - T_e) \quad (10)$$

Where U is the heat transfer coefficient J/(s·m²·K), S is the wetted surface area, m² and T_e is the ambient temperature.

Combine the Equation (8) and (9) and according to the system energy balance, then

$$MC_p \frac{dT}{dt} = \Delta H_{rxn} M^n A \exp\left(-\frac{E_a}{RT}\right) - US(T - T_e) \quad (11)$$

When the temperature T equals to T_{NR} (T_{NR} is the temperature of no return [K], at which the rate of heat generation of a reaction or decomposition is equal to the maximum rate of cooling available [25])

$$MC_p \frac{dT}{dt} = 0 \quad (12)$$

Therefore,

$$\Delta H_{rxn} M^n A \exp\left(-\frac{E_a}{RT_{NR}}\right) = US(T_{NR} - T_e) \quad (13)$$

Differentiating both sides of Equation (12) regarding T_{NR} ,

$$\frac{\Delta H_{rxn} \cdot M^n E_a A \exp[-E_a/(RT_{NR})]}{RT_{NR}^2} = US \quad (14)$$

Combining equation (12) and (13), then

$$T_a = T_{NR} - \frac{RT_{NR}^2}{E_a} \quad (15)$$

T_a is the self-accelerating decomposition temperature (SADT), K.

For the UN25 kg package, $U = 2.83 \text{ J}/(\text{s} \cdot \text{m}^2 \cdot \text{K})$, $S = 0.4812 \text{ m}^2$ [26]. Using Matlab nonlinear least-squares (lsqnonlin) function to solve the T_{NR} from Equation (13) and further calculate the T_a using Equation (21). The calculated results of the T_{NR} and SADT for DSC, ARSST and APTAC are listed in Table 6. The results for ARSST and DSC are similar. The APTAC results are higher values due to the equipment limitations for the temperature measurement and the high thermal inertia (ϕ). The thermal inertia factor of APTAC is larger than DSC's and ARSST's. After the heater in the APTAC stops working due to the shut-down criteria, the heat generated from the reaction will be largely consumed by the test cells. Therefore the calculated T_{NR} and SADT will be larger.

Table 6

T_{NR} and SADT calculation of 3 different types of calorimeters for UN 25 kg package

Calorimeter	T_{NR} (K)	SADT (K)
DSC (ref. [9])	614	597
ARSST (Test No. 2)	638	621
APTAC (Sample A)	665	646

4. Conclusions

According to the ARSST data, 2-NT decomposes between 300 to 350 °C and the heat of the reaction is about 74 kJ/mol. If the sample size is larger, then the observed onset temperature will be lower and if the initial pressure is higher, then the onset temperature will be lower. Also, from the temperature increase rate profiles, 2 peaks exist which may indicate at least 2 distinct different reactions happen during the decomposition of 2-NT.

According to the APTAC data, the self-heat rate of 2-NT is as high as 6889 °C/min which is consistent with the severe consequences when the decomposition happens. The onset temperature from APTAC is 279 °C which is lower than the DSC and ARSST results. Under an external fire circumstance, 2-NT can decompose quickly and cause a runaway reaction and thermal explosion. The effective thermokinetics are determined by the thermal curve of APTAC tests with the fitting correlations larger than 99%. The reaction order of the 2-NT decomposition is determined to be 0.1 and the reaction can be treated as zero-order reaction.

To sum up, this study provides experimental data of 2-NT decomposition for different sample sizes and initial pressures using two different types of calorimeter (ARSST and APTAC). Results from the tests provide evidence to show that 2-NT is a very dangerous material. Also, a simulated method is employed to establish the kinetic parameters (E_a , A , ΔH) and then compared with the data obtained from experiments. Later, kinetic parameters and heat of reactions from different calorimeters are used to estimate the safety parameters (T_{NR} , SADT). All of the related hazard-

information in this study helps to determine safer operation conditions for handling, storage and transportation of 2-NT in the chemical process industry.

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