

Study on the thermal decomposition kinetics of DNTF

Jiangshan Gu¹, Lu Liu¹, Huanhuan Chen¹, Wanghua Chen¹, Zichao Guo¹ and Liping Chen^{1*}

¹ Department of Safety Engineering, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing Jiangsu 210094, China

Abstract. 3,4-Dinitrofurazanyluroxan (DNTF) is a representative of the third-generation energetic materials with complex thermal decomposition behavior. Understanding thermal decomposition process of DNTF is of great significance for the safety of its production, storage and use. In this paper, the dynamic differential scanning calorimetry (DSC) test is carried out to study its thermal decomposition characteristics. The quench and reheat experiments and isothermal tests were performed to determine the types of decomposition reactions. A four-step consecutive reaction model, $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$, where each step is an N-order reaction was established for the decomposition process. The established kinetic models were verified by 250°C isothermal test.

1 Introduction

Understanding the thermal decomposition kinetics of energetic materials is of great significance to the safety of storage and transportation. As the third-generation energetic material, DNTF has the characteristics of high energy density, high standard enthalpy of formation, and high nitrogen content [1]. The structure is shown in Figure 1.

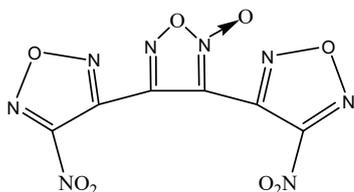


Figure 1. Molecular structure of DNTF.

The thermal decomposition kinetics of DNTF has been extensively studied. F. Q. Zhao et al. [2] obtained the most probable mechanism function $f(\alpha)=3(1-\alpha)^{2/3}$ of the main peak of DNTF by matching a single dynamic curve with 41 mechanism functions, and the corresponding activation energy and pre-exponential factor are 177.03 kJ mol⁻¹ and 1013.68 s⁻¹, respectively. V. P. Sinditskii et al. [3] found that there is a secondary decomposition reaction of DNTF, and established a two-step reaction model based on the isothermal DSC curve in the liquid phase, which includes two independent first-order reactions. J. Gao et al. [4] found that the TFO and BFO produced during the production process slightly reduce the activation energy of DNTF, indicating that the existence of impurities reduces the thermal stability of DNTF to a certain extent. However, existing researches mostly use Kissinger method or Ozawa method to solve their kinetic parameters, or use a single-step reaction model to approximate their thermal

decomposition process, leading to deviations in the calculation results. In order to obtain more accurate kinetics of energetic materials, a multi-step reaction model must be established to describe its thermal decomposition behavior more accurately.

In this paper, Isothermal tests and quench and reheat tests will be carried out to determine the reaction type of each exothermic peak of DNTF. Then a multi-step reaction model will be established and verified by comparison of prediction curve and experimental curve of isothermal experiments.

2 Materials and Methods

DNTF is produced by Gansu Yinguang Chemical Industry Co., Ltd., and its appearance is light yellow particles. The particle size range is 0.15-0.22 mm.

DSC used in this article is manufactured by METTLER TOLEDO (DSC-1). The sensitivity of the instrument is 0.04 μW, and it has been calibrated with indium and zinc before the experiment. Disposable closed gold-plated crucibles were used in the test, the maximum pressure of which can reach 20 MPa. N₂ was applied as test atmosphere (50 mL s⁻¹) during the DSC test. In the dynamic test, the heating rate was 1, 2, 4, 8K min⁻¹, and the sample mass was 1.34, 1.34, 1.33, 1.34 mg, respectively. The temperature range is 120-400°C. In the isothermal test, DNTF was performed at 230°C, 250°C and 280°C. The sample mass was 1.36 mg, 1.36 mg, and 1.40 mg, respectively.

In the quench and reheat experiment, the sample was first heated to 240, 275°C at 4 K min⁻¹ to make it reach different conversion rate of decomposition. The sample mass was 1.35, 1.35 mg, respectively. The heating process here is defined as the first stage test, and these first reached temperatures are called as the interruption temperature.

* Corresponding author: clp319@njust.edu.cn

After that, the samples were cooled to the start temperature 120°C. Finally, these samples were heated again from 120°C to 400°C at the same heating rate until the sample decomposed completely, which is called as the second stage test.

3 Results & Discussion

3.1 Dynamic DSC test

Dynamic curves of DNTF at different heating rates are shown in Figure 2. The relevant parameters are listed in Table 1. It can be seen from Figure 2 that the dynamic DSC experimental curve of DNTF clearly shows three exothermic peaks, which are called P1, P2, and P3. Studies have shown that the decomposition of P2 is the rupture of the furuzan ring, and the decomposition of P3 is the decomposition of furuzan fragments at high temperatures [3]. The onset temperature and peak temperature of DNTF move to higher temperature with the increase of the heating rate. Due to the melting point of DNTF is 110°C, the decomposition of DNTF is in liquid phase.

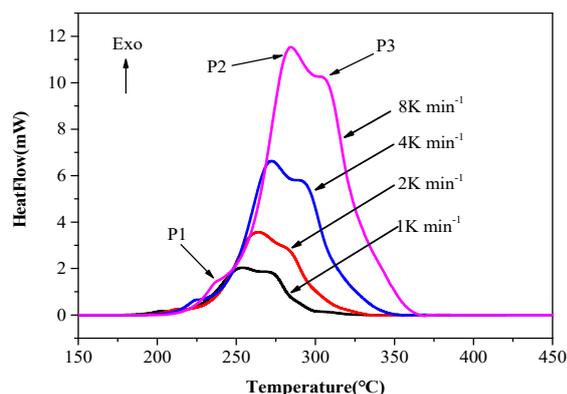


Figure 2. Dynamic DSC experimental curves of DNTF

Table 1. Dynamic DSC results of DNTF at different heating rates

β (K min ⁻¹)	T_0 (°C) _a	T_{p1} (°C) _b	T_{p2} (°C) _b	T_{p3} (°C) _b	Q (kJ kg ⁻¹)
1	182.8	203	254	272	4502
2	185.8	212	264	280	4531
4	196.3	224	273	291	4568
8	200.6	236	283	302	4514

^a T_0 refers to the temperature at which the DSC curve deviates from the baseline. ^b T_{p1} , T_{p2} , T_{p3} refer to the peak temperature of peak1-peak3.

3.2 Isothermal DSC test

The discrimination of acceleration reaction, deceleration reaction and S-type reaction has a great influence on the results of kinetic parameters. ICTAC recommends doing at least one isothermal experiment after the dynamic test is completed, because the isothermal reaction can easily distinguish whether the reaction is an accelerated, decelerated, or S-shaped reaction. The experimental results are shown in Figure 3 (a) (c) (e). The isothermal curves shown were all subtracted the blank curve. After

the isothermal test, dynamic test on the remaining materials were performed to determine whether all reactions were triggered at the isothermal temperature. The experimental results are shown in Figure 3(b) (d) (f).

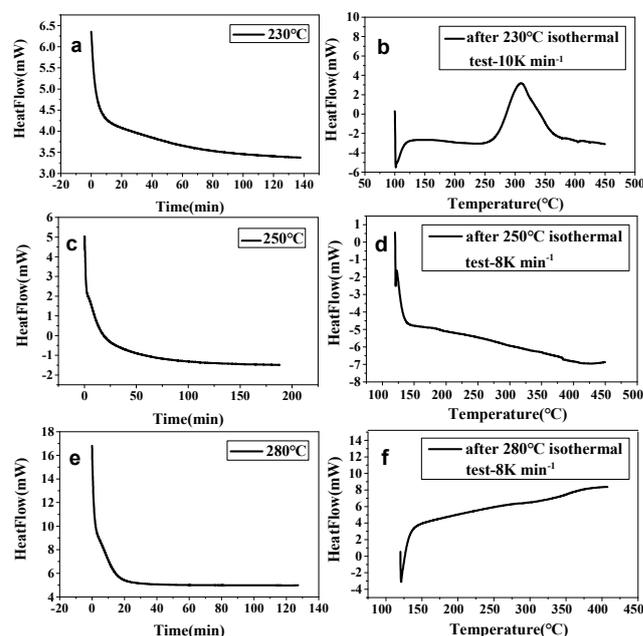


Figure 3. Isothermal curves of DNTF at different isothermal temperatures and dynamic tests after isothermal tests.

It can be seen from Figure 3(a) that the isothermal exothermic rate of DNTF at 230°C shows a downward trend, which conforms to the law of deceleration type reaction. The deceleration reaction is usually expressed by the N-order reaction equation. In addition, there is an obvious turning point in Figure 3(a), which may be the overlap of two N-order reactions. Comparing with the dynamic curve of 1K min⁻¹, it can be found that 230°C is located at the initial stage of the P2 reaction after the end of the P1 reaction. Under isothermal conditions, the onset temperature of each reaction may be lower, which means that the reaction of P1 and P2 may be triggered at 230°C. A dynamic test with a temperature range of 100-450°C and a heating rate of 10K min⁻¹ was performed on the material after the isothermal reaction at 230°C. It can be found that the material after the isothermal test still has an exothermic heat of 1641.73 kJ kg⁻¹. This means that DNTF was not completely decomposed at 230°C, which also reflects the limitation of the narrow temperature range of the isothermal experiment.

The isothermal temperature was increased to 250°C, and the results obtained are shown in Figure 3(c). The heat release rate of DNTF still shows a downward trend at 250°C, which conforms to the decelerating reaction. Moreover, the isothermal curve at 250°C has two turning points, which may include three reaction steps. A dynamic test with a temperature range of 120-450°C and a heating rate of 8K min⁻¹ was performed on the material after 250°C isothermal test. The result is shown in Figure 3(d). From Figure 3(d), it can be seen that the substance after isothermal test is basically not exothermic, which proves that the temperature of 250°C has initiated all reactions.

Then the isothermal temperature was increased to 280°C, and the results obtained are shown in Figure 3(e). The heat release rate of DNTF at 280°C still shows a downward trend, and the isothermal heat release is still large. Compared with the dynamic curve of 1 K min⁻¹, it can be found that the temperature of 280°C is at the half-peak height of the P3 reaction rate decrease section, but the isothermal curve at 280°C still has a turning point. It is speculated that in addition to the reaction corresponding to P3, there may be another step-P4 involved here. From Figure 3(f), it can be seen that the curve after isothermal test does not show exotherm. It can be concluded that the isothermal temperature of 280°C is sufficient for the subsequent reaction to exotherm completely.

3.3 Quench and reheat experiment

Quench and reheat experiments are used to assist in verifying whether the decomposition peak of DNTF has autocatalytic characteristics [5][6]. This method can't determine the reaction type of P1 because the heat release of P1 is small and the peak height is low. It is easy to cause the reaction to end in the second stage due to the temperature overshoot. Therefore, this method is not used to identify the autocatalytic characteristics of P1.

DNTF is heated to two different interruption temperatures of 240°C and 275°C to simulate samples that have experienced different degrees of thermal history. Figure 4 shows the comparison of the second stage curve with the original curve with a heating rate of 4K min⁻¹ at different interruption temperatures. The relevant parameters are listed in Table 2.

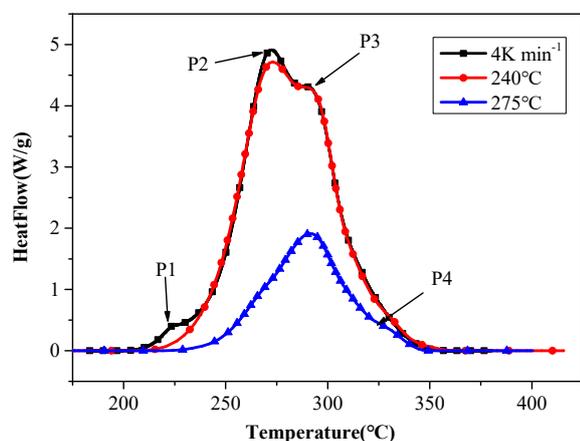


Figure 4. Comparison of the second stage curve at different interruption temperatures and the original curve at the heating rate of 4K min⁻¹.

Table 2. Peak temperatures comparison of the second stage test and the original curve

β (K min ⁻¹)	Interruption temperature (°C)	T _{p2} (°C)	T _{p3} (°C)
4	-	272.7	290.9
4	240.0	273.1	290.8
4	275.0	-	291.4

It can be seen from Figure 4 that when interrupted at 240°C, P1 disappeared in the second stage DSC curve,

indicating that during the first stage (120°C-240°C) the reaction of P1 has totally completed. The peak height of P2 was decreased, which proves that the reaction of P2 has been initiated in the first stage, and part of the reaction product of P2 has been formed. According to the data in Table 2, the peak temperature of P2 in the second stage test has no obvious change compared with the original curve, indicating that the P2 reaction product produced in the first stage does not have a catalytic effect on the reaction of P2, so it is classified as an N-order reaction. In the same way, the peak height of the P3 in the second stage test has no change compared with the original curve, indicating that the P3 reaction has not been initiated in the first stage, and the interruption temperature needs to be raised and judged again.

Increase the interruption temperature to 275°C, which is close to the peak temperature of P2. The result of the second stage test is shown in Figure 4. Comparing the curve of the second stage test at 275°C interruption temperature with the original curve, the peak height of P3 is greatly reduced, indicating that the reaction degree of P3 in the first stage test is deep. Considering the data in Table 2, it can be seen that the peak temperature of P3 in the second stage test was basically not changed, so it is classified as an N-order reaction. In addition, there is a shoulder peak at 272°C and 325°C, respectively. The shoulder peak at about 272°C is due to the incomplete reaction of P2 in the first stage test. A possible explanation for the shoulder peak at about 325°C is that P3 is not a single-step reaction. There may be a "hidden" P4 near 325°C, but covered by P3 in the original curve. In the second stage test at 275°C interruption temperature, due to different reaction processes of P3 and P4, the degree of peak height reduction is also different, so that the P4 appears.

3.4 Kinetic parameter evaluation

3.4.1 Determination the activation energy by Friedman method

Friedman method is used to preliminarily estimate the variation range of the activation energy during the thermal decomposition of DNTF. The result is shown in Figure 5.

This method is based on the isoconversional principle, that is, the reaction rate is only a function of temperature at a constant conversion.

Usually the reaction rate is regarded as a function related to temperature and conversion. The dependence of the reaction rate on temperature is expressed by the Arrhenius equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A \exp\left(\frac{-E}{RT}\right)f(\alpha) \quad (1)$$

Where E is the activation energy, R is the gas constant, and A is the pre-exponential factor, f(α) is the Reaction model.

When α=constant, f(α) is also a constant, then the logarithm of equation (1) can be obtained:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (2)$$

The subscript i represents different temperature control methods, and $T_{\alpha,i}$ represents the temperature when the conversion rate α is reached under the i -th temperature control method. For any value of α , the value of E_{α} can be obtained from the slope of $\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i}$ and $1/T_{\alpha,i}$ after linear fitting. Under linear temperature increase condition, equation (2) can be transformed into:

$$\ln\left[\beta_i\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right] = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (3)$$

Where β_i corresponds to different heating rate.

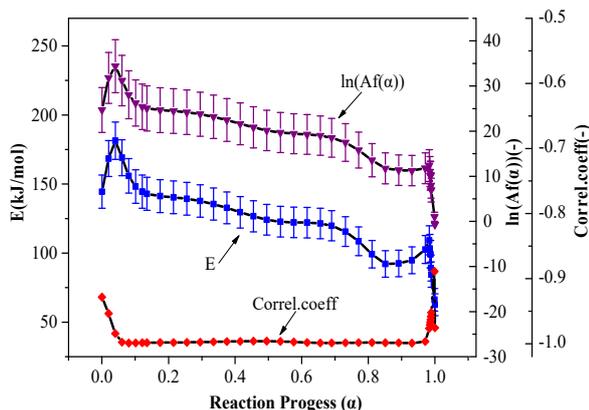


Figure 5. Apparent activation energy, $\ln(Af(\alpha))$ vs. conversion for DNTF

The kinetic parameters in the early and late stages of the reaction are greatly affected by small errors in the baseline, and instrument fluctuations will also cause distortion of the kinetic parameters, resulting in an increase in the correlation coefficient. Therefore, only the fluctuation trend of activation energy in the range of 0.05~0.95 is considered. It can be seen from Figure 5 that the activation energy shows a slow downward trend in the interval of $\alpha=0.05\sim 0.1$, ranging from 175.2 kJ/mol to 148.2 kJ/mol, which is approximately regarded as a single-step reaction. In the interval of $\alpha=0.1\sim 0.5$, the activation energy decreases from 148.2 kJ/mol to 124.1 kJ/mol, which changes in a small range, so it is approximately considered as a single-step reaction. Between $\alpha=0.5\sim 0.7$, the activation energy presents a plateau and stabilizes at about 120.0 kJ/mol. This stage can also be considered as a single-step reaction. Then in the interval of $\alpha=0.7\sim 0.95$, the activation energy showed a significant decrease, from 119.8 kJ/mol to 92.5 kJ/mol and then increasing to 102.6 kJ/mol, the range of change was close to 30% of the average, which proves that the late stage of DNTF decomposition may include multi-step reactions [7]. Combined with phenomena such as the shoulder peak appearing at 325°C in the 275°C quench and reheat experiment, it can be seen that the decomposition of DNTF includes at least four reactions, as shown in Figure 6.

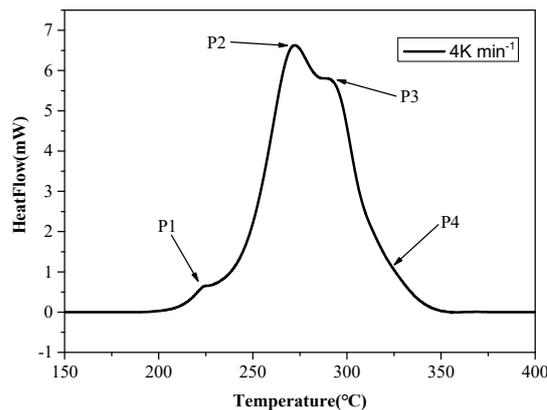
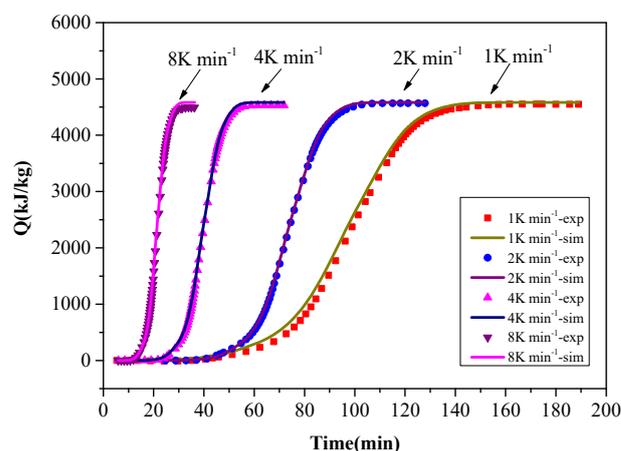


Figure 6. Schematic diagram of the four-step reaction of DNTF

3.4.2 Determination the reaction kinetic model

From the above isothermal test and quench and reheat experiment, it can be known that the decomposition reaction types of DNTF are all N-order reaction. Observing Figure 7(a), it can be seen that the heat release of DNTF does not increase and decrease regularly with the change of heating rate β [8]. Therefore, the consecutive reaction model of $A\rightarrow B\rightarrow C\rightarrow D\rightarrow E$ was used to describe the decomposition kinetics of DNTF. Use the Fork module of the TSS software to perform a nonlinear fitting of the heat release time curve and the heat release rate time curve. The results are shown in Figure 7. The relevant parameters of the model are shown in Table 3. It can be found that the built multi-step reaction model has a good effect on the simulation and reproduction of the multi-peak curve. The correlation coefficient of heat release time curve fitting is 0.9998, and the correlation coefficient of heat release rate time curve fitting is 0.9972.



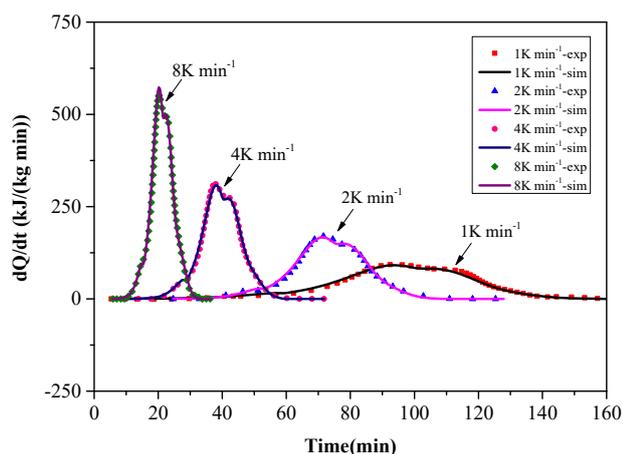


Figure 7. Comparison of the kinetic model fitting curve and the experimental curve. (a. Heat release vs time diagram at different heating rates; b. Heat release rate vs time diagram at different heating rates)

Table 3. Kinetic parameters of reaction model for DNTF

Kinetic parameters	A→B		B→C	
	$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n$	$\ln(k_0)$	$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n$	$\ln(k_0)$
$\ln(k_0)$	$\ln(s^{-1})$	36.1±0.1	29.1±0.1	
E	$kJ \cdot mol^{-1}$	171.2±0.1	154.2±0.1	
n	—	0.57±0.01	0.72±0.01	
Q	$J \cdot g^{-1}$	142±1	1399±1	
Kinetic parameters	C→D		D→E	
	$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n$	$\ln(k_0)$	$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E}{RT}\right)(1-\alpha)^n$	$\ln(k_0)$
$\ln(k_0)$	$\ln(s^{-1})$	23.7±0.1	13.7±0.1	
E	$kJ \cdot mol^{-1}$	135.4±0.1	93.4±0.1	
n	—	0.90±0.01	0.97±0.01	
Q	$J \cdot g^{-1}$	1949±1	1091±1	

Comparing the activation energy obtained by the model fitting method and the Friedman method, it is found that the activation energy obtained by model fitting method are all within the range of $E \sim \alpha$ calculated by Friedman's method, and the trend is consistent. It shows that although the Friedman method is based on the assumption of a single-step reaction, it still gives a reasonable range of activation energy when it is applied to a multi-step reaction.

3.5 Kinetic model verification based on isothermal data

Based on the established consecutive reaction model of $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$, the isothermal curve at 250°C was predicted and compared with the experimental curve. The comparison figure of the heat release-time curve is shown in Figure 8. The comparison figure of the heat release rate-time curve is shown in Figure 9.

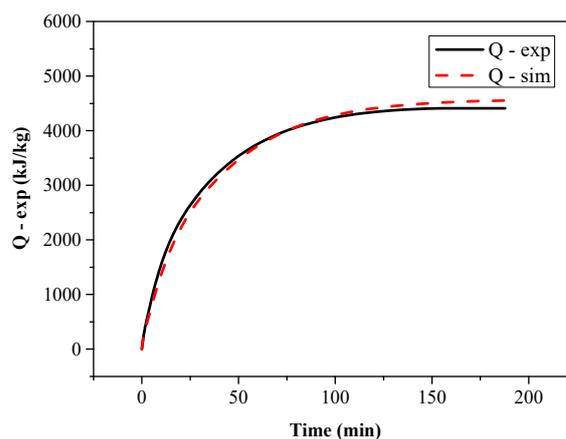


Figure 8. Comparison of heat release-time prediction curve and experimental curve at 250°C isothermal test.

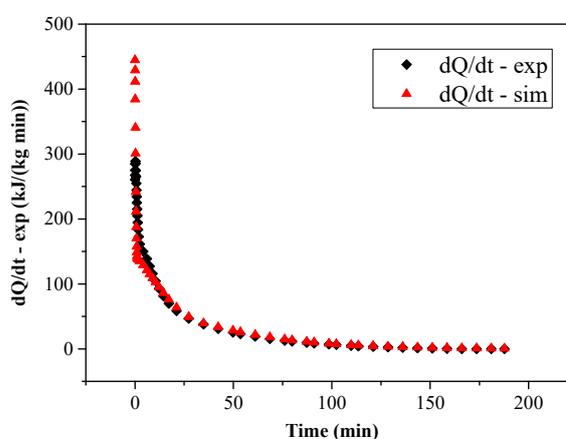


Figure 9. Comparison of heat release rate-time prediction curve and experimental curve at 250°C isothermal test.

From Figure 8, it can be seen that the exothermic heat release at 250°C isothermal temperature is about 4400 kJ kg⁻¹, which is less than the exothermic heat of the DSC dynamic experiment, indicating that the sample temperature has been partially decomposed before reaching 250°C. This part of the heat release is not recorded in the DSC isothermal curve, so the experimental heat release will be slightly lower than the predicted value. Generally speaking, the predicted curve of heat release rate-time at 250°C in Figure 9 is consistent with the experimental curve. The two turning points of the experimental curve are also reflected in the predicted curve. In the early stage of isothermal test, there will be a part of heat loss due to the non-zero conversion rate of DNTF, which leads to deviations from the predicted curve. But in general it can be considered that the predicted curve is close to the experimental curve, which proves the rationality of the multi-step kinetic model.

4 Conclusion

In this paper, a disposable gold-plated crucible was used to perform DSC tests on DNTF samples with different temperature control procedures. The conclusions are as follows:

(1) DSC test results show that the thermal decomposition of DNTF contains three obvious

exothermic peaks P1, P2, P3, which shows that the thermal decomposition of DNTF includes at least three reactions. Based on isothermal tests and quench and reheat experiments, all of the decomposition peaks were described by N-order reaction model. Moreover, the possibility of the existence of P4 was inferred.

(2) According to Friedman method, the activation energy of DNTF ranges from 92.5 kJ/mol to 175.2 kJ/mol, and changes greatly when $\alpha = 0.7\sim 0.9$. It means that there is a further P4 decomposition reaction in the late stage of decomposition.

(3) The multi-step kinetic model $A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$ of DNTF was established using the model fitting method. All steps were described by the N-order reaction model. The activation energy of each step is within the range calculated by Friedman method.

(4) The isothermal curve at 250°C predicted based on the kinetic model is consistent with the experimental curve, which verifies the rationality of the kinetic model.

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