Research on thermal decomposition of 1,3,5-trinitro-1,3,5-triazinane based on differential scanning calorimetry

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Abstract: In order to test the thermal decomposition of 1,3,5-trinitro-1,3,5-triazinane (RDX), the linear temperature rise experiment of RDX was carried out by differential scanning calorimeter under different heating rate conditions. The kinetic calculation of RDX thermal decomposition curve was carried out by Kissinger and Ozawa methods, respectively, and the thermal analysis software was used to calculate the parameters such as self-accelerating decomposition temperature. The results show that the initial decomposition temperature range, decomposition peak temperature range, and decomposition completion temperature range of RDX are 208.4 — 214.2, 225.7 — 239.3 and 234.0 — 252.4 ℃, respectively, and the average decomposition enthalpy is 362.9 J·g^{-1}. Kissinger method was used to calculate the DSC experimental data of RDX, the apparent activation energy obtained is 190.8 kJ·mol^{-1}, which is coincident with the results calculated by Ozawa method at the end of the reaction, indicating that the apparent activation energy calculated by the two methods is relatively accurate. When the packaging mass values are 1.0, 2.0 and 5.0 kg, respectively, the self-accelerating decomposition temperatures are 97.0, 93.0 and 87.0 ℃, respectively, indicating that with the increase of packaging mass, the self-accelerating decomposition temperature gradually decreases, and the risk increases accordingly.

Key words: 1,3,5-trinitro-1,3,5-triazinane (RDX); differential scanning calorimetry (DSC); thermal decomposition; kinetics

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0 Introduction

1,3,5-trinitro-1,3,5-triazinane (RDX), as one of the most commonly used explosives, is an important part of gun and solid propellants. It has good detonation performance, and widely used in the field of energetic materials[1-3]. Therefore, in recent years, the thermal decomposition and thermal stability of RDX have been the focus of research. Since the middle of last century, the traditional research technology of gas decomposition products and thermogravimetry curve has been adopted by researchers. In addition, high-pressure differential scanning calorimetry, isotope labeling and isotope effect have also been widely used in the field of thermal decomposition. Many technical methods have been used to study the thermal decomposition process and thermal stability of RDX, and many important conclusions for production and transportation process have guiding significance to reduce the occurrence of accidents. Lee et al.[4-6] studied the thermal decomposition of RDX by the thermal infrared technology, expecially the thermal decomposition of RDX under the influence of factors such as sample mass, heating rate and dynamic and static high pressure using PDSC and TG-DTG technology. Jin et al. explored the thermal decomposition process of RDX, 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocan (HMX) by differential thermal analysis (DTA), and found that there is a linear correlation between the decomposition rate constant and the combustion rate inhibition coefficient under different pressures[7]. Ding et al.[8-10] studied the effect of TNT on the thermal decomposition process of RDX. The results show that TNT can improve the thermal stability and the safety of RDX to a certain extent. A large number of existing studies contribute to a deep understanding of RDX, but there are still some deficiencies in the thermal decomposition of RDX based on differential scanning calorimetry experiments. Here we intend to test the thermal decomposition of RDX by differential scanning calorimeter to obtain the thermal decomposition parameters and change characteristics of RDX at different heating rates, in order to make some supplement to the thermal decomposition test of

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RDX.

1 Experimental

1.1 Sample

When the percentage of particle size distribution reaches 50.0%, the corresponding particle size ($D50$) of RDX is 20.0 μm.

1.2 Equipment and experimentation

Differential scanning calorimeter (DSC) was produced by SETARAM Company, France, and its temperature range is 0 — 700.0 ℃ and program-controlled temperature scanning rate is 0.1 — 100.0 ℃/min, with the functions of rapid cooling and heating and a high-pressure crucible. The protective gas is high-purity nitrogen, and the flow rate is 40.0 ml/min.

The experimental heating rates are set at 5.0, 10.0, 15.0 and 20.0 ℃/min, respectively, and the dosage of sample is 0.5 mg.

2 Results and discussion

2.1 Thermal decomposition of RDX

The linear temperature rise experiment of RDX of DSC is shown in Fig. 1, and Table 1 shows the experimental conditions and results.

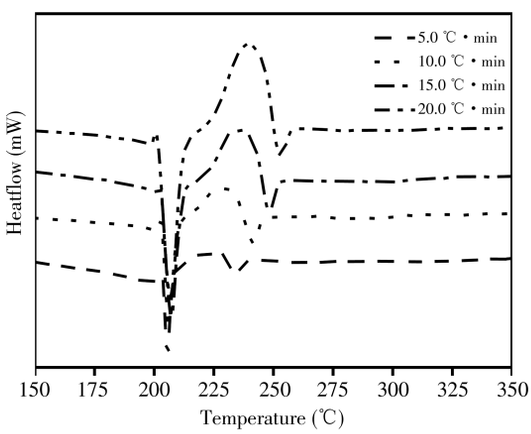

Fig. 1 DSC experimental curves of RDX

It can be seen from Fig. 1 and Table 1 that the initial decomposition temperature (T_{onset}), the exothermic peak temperature (T_{peak}) and the decomposition completion temperature (T_{offet}) of RDX shift to the high temperature direction with the increase of heating rate, which is caused by the thermal hysteresis phenomenon during the thermal decomposition process of RDX[11]. The initial decomposition temperature of RDX is 208.4—214.2 ℃, the peak decomposition temperature of RXD is 225.7—239.3 ℃, the decomposition completion temperature of RXD is 234.0—252.4 ℃, and the average decomposition enthalpy (ΔH_r) is 362.9 J/g.

Table 1 Characteristic parameters of DSC experiments of RDX

Experiment	β (℃/min)	T_{onset} (℃)	T_{peak} (℃)	T_{offet} (℃)	ΔH_r (J/g)
DSC	5.0	208.4	225.7	234.0	337.3
	10.0	209.9	228.3	241.3	342.4
	15.0	213.0	237.5	248.6	357.8
	20.0	214.2	239.3	252.4	413.9

2.2 Kinetic analysis

Based on the DSC experimental data of RDX in Section 2.1, the thermal decomposition kinetics of RDX was analyzed by Kissinger method[12] and Ozawa method[13], respectively. Using Kissinger method, the slope and intercept of the straight line are apparent activation energy (E_a) of RDX and pre-exponential factor (A), respectively. Using Ozawa method, based on the experimental curves under different heating rates, selecting the same reaction conversion rate to make the corresponding relationship curve, the apparent activation energy of RDX can be obtained. This method cannot get the value of $f(\alpha)$, only gets the product of A and $f(\alpha)$, which avoids many assumptions in the reaction process and makes the calculation results more universal[14].

Fig. 2 lists the calculation results of RDX by the above two kinetics analysis methods. It can be seen from Fig. 2 the apparent activation energy Kissinger method calculated is 190.8 kJ · mol^{-1}. In order to eliminate the effect of baseline selection and instrument noise in the reaction process, the conversion rate is 0.05—0.95.

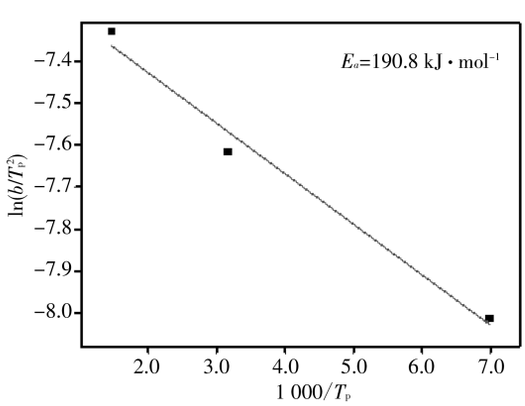

Fig. 2 Fitting curve of apparent activation energy (Kissinger)

It can be seen from Fig. 3 that the apparent activation energy of RDX calculated by Ozawa

method is larger at the initial stage of the reaction. As the reaction proceeds, the apparent activation energy gradually decreases until the end of the reaction. This is because the thermal decomposition of RDX is a complex reaction, and there are different reactions at different reaction stages. During the reaction process, some substances were produced to promote the reaction and reduce the apparent activation energy[15-16]. The apparent activation energy of RDX calculated by Kissinger method basically coincides with the result calculated by the Ozawa method at the end of the reaction, indicating that the calculated apparent activation energy is more accurate.

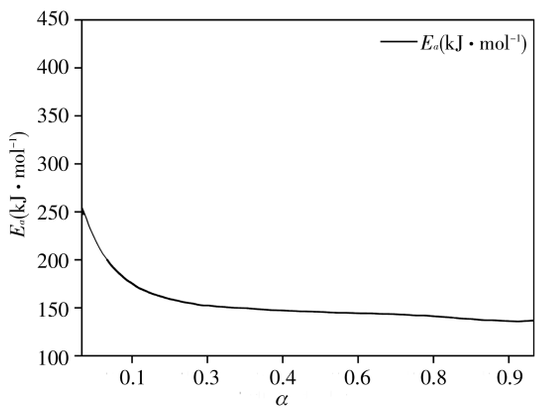

Fig. 3 Relation curve between E and conversion rate α (Ozawa)

Based on the DSC curve of RDX, RDX was predicted and simulated by advanced thermal analysis software. Advanced kinetics software can predict the degree of thermal hazard of the substance. Four thermal decomposition curves of RDX under different heating rates in Fig. 1 were imported into the software, and the reaction process, reaction rate experiment and simulation curves of RDX were obtained. Then the self-accelerating decomposition temperature of RDX was calculated by the simulation curve, and the experimental process and simulation curve of reaction process and reaction rate were obtained, and the self-accelerating decomposition temperature of RDX was calculated by the simulation curves. The decomposition peak temperature of RDX on the simulation curve is basically the same as that obtained by experiment. Finally, based on the simulation curves of RDX, the self-accelerating decomposition temperature of RDX was calculated when the packaging mass values were 1.0, 2.0 and 5.0 kg, respectively.

Self-accelerating decomposition temperature is an important parameter to evaluate the safety of thermal decomposition of RDX[17-18]. The calculation results of the self-accelerating decomposition temperature of RDX are shown in Figs. 4 — 6. It can be seen that when the packaging mass values are 1.0, 2.0 and 5.0 kg, respectively, the corresponding self-accelerating decomposition temperature values are 97.0, 93.0 and 87.0 ℃, respectively. With the increase of packaging mass, the self-accelerating decomposition temperature gradually decreases. The heat generated in the thermal decomposition process of RDX is more difficult to exchange with the outside world, and the risk also increases. The smaller the packaging mass, the easier the heat exchange with the external environment, thus the safety increases.

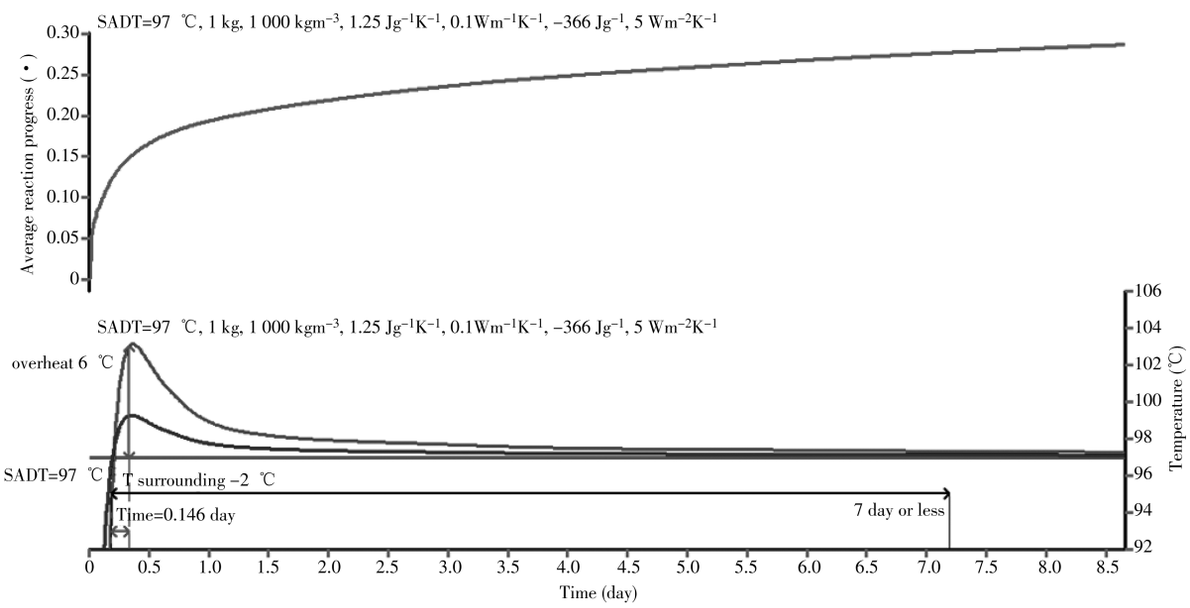

Fig. 4 Calculation results of RDX self-accelerating decomposition temperature (1.0 kg)

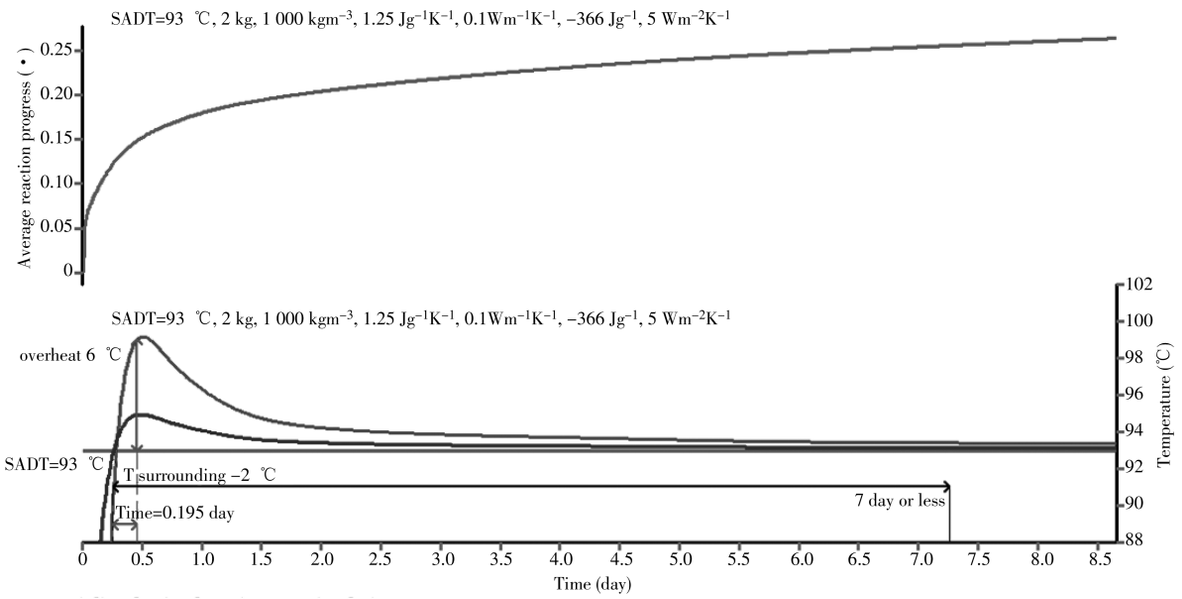

Fig. 5 Calculation results of RDX self-accelerating decomposition temperature (2.0 kg)

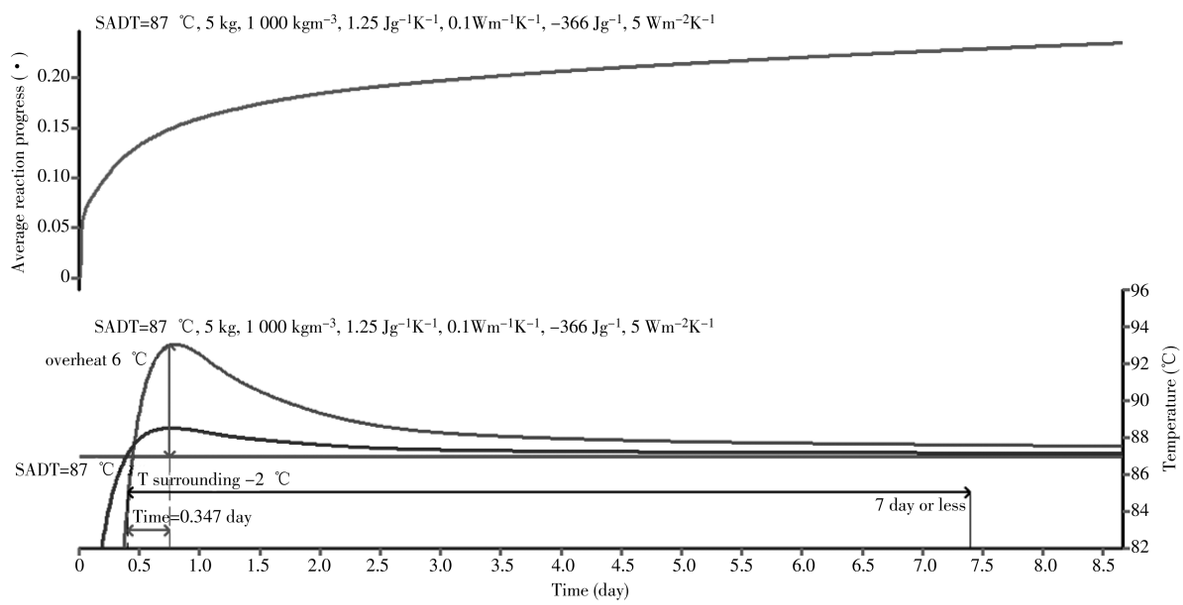

Fig. 6 Calculation results of RDX self-accelerating decomposition temperature (5.0 kg)

3 Conclusions

1) The initial decomposition temperature, decomposition peak temperature and decomposition completion temperature of DSC experiment of RDX are 208.4 — 214.2, 225.7 — 239.3 and 234.0 — 252.4 ℃, respectively, and they all move toward high temperature direction as heating rate increases. The average decomposition enthalpy is 362.9 J/g.

2) The apparent activation energy of RDX calculated by Kissinger method is 190.8 kJ/mol. The apparent activation energy of RDX calculated by Ozawa method is larger at the beginning of the reaction. With the reaction going on, the apparent activation energy gradually decreases until reaction ends. The results calculated by Kissinger method and Ozawa method coincide at the end of reaction, which means the activation energy calculated by the two methods is more accurate.

3) When the packaging mass values are 1.0, 2.0 and 5.0 kg, respectively, the self-accelerating decomposition temperature values are 97.0, 93.0 and 87.0 ℃, respectively. With the increase of packaging mass, the self-accelerating decomposition temperature gradually decreases, and risk increases too.

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基于差示扫描量热实验对 1,3,5-三硝基-1,3,5-三氮杂环己烷热分解的测试研究

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摘 要: 为了对 1,3,5-三硝基-1,3,5-三氮杂环己烷 (RDX)的热分解进行测试研究, 通过差示扫描量热仪在不同升温速率条件下对 RDX 进行线性升温实验,采用 Kissinger 法和 Ozawa 法分别对 RDX 的热分解曲线进行动力学计算, 并结合热分析软件计算自加速分解温度等参数。结果表明, RDX 的初始分解温度、分解峰温、分解完成温度范围分别为 208.4—214.2 ℃、225.7—239.3 ℃和 234.0—252.4 ℃, 分解焓平均为 362.9 J·g^{-1}。采用 Kissinger 法对 RDX 的 DSC 实验数据进行计算, 得出的表观活化能为 190.8 kJ·mol^{-1}, 与 Ozawa 法计算的结果在反应末期重合, 表明两种方法计算的表观活化能较为准确。在包装质量分别为 1.0、2.0 和 5.0 kg 时, 其自加速分解温度为 97.0、93.0 和 87.0 ℃, 表明随着包装质量的增加, 自加速分解温度逐渐降低, 危险性随之增大。

关键词: 1,3,5-三硝基-1,3,5-三氮杂环己烷; 差示扫描量热仪; 热分解; 动力学

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