Properties and characterization of 1-methy-4, 5-dinitroimidazole

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Abstract: X-ray diffraction (XRD), differential scanning calorimeter (DSC) and impact sensitivity instrument were used to characterize the properties of 1-Methyl-4, 5-dinitroimidazole (MDNI). Furthermore, specific heat capacity, thermal kinetic parameters, thermal decomposition reaction rate constant, critical explosion temperature and the drop height for impact initiation of MDNI were calculated and analyzed. The results show that MDNI is well-crystallized. The melting point of MDNI is about 74 ℃, and the specific heat capacity of MDNI is 9.314 4 J/(g·K) and 10.596 0 J/(g·K) when the temperature is 60 ℃ and 90 ℃, respectively. The apparent activation energy and pre-exponential factor of MDNI are calculated as 81.62 kJ/mol and 6.78×10^{7} s^{-1}, respectively. The relationship between thermal decomposition reaction rate constant of MDNI and temperature is $\log k=7.83-4268.11/T$. The critical temperature of MDNI thermal explosion is 234.86 ℃. The drop height for impact initiation of MDNI is 95.3 cm.

Key words: 1-Methyl-4, 5-dinitroimidazole; X-ray diffraction (XRD); thermal decomposition; kinetic; impact sensitivity

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0 Introduction

Trinitrotoluene (TNT) has mature synthesis process, suitable melting and freezing point for casting, low mechanical sensitivity and moderate detonation energy performance[1]. Melt cast explosive, which was made of liquid melt cast carrier (TNT) and high energy solid explosive compound (RDX, HMX and NTO) was widely used in the ammunition[2-4]. With the dynamic development of hi-tech and high modern weapons, traditional melt cast explosive with TNT as its only liquid carrier can not meet the requirements of high energy density, low vulnerability and environment adaptability for weapons ammunition[5-6]. Thus, the new liquid melt cast carriers were developed to replace TNT in whole or in part by the scientific researchers, for example, 3, 4-Dinitrofurazanofuroxan (DNTF)[7-9], 2, 4-Dinitroanisole (DNAN)[10-11], 3, 4-Dinitropyrazole (DNP)[12-13], 1,3,3-Trinitroazetidine (TNAZ)[14-15], 1-Methyl-3, 4, 5-trinitropyrazole (MTNP)[16], 1-Methyl-2, 4, 5-trinitroimidazole (MTNI)[17] and so on. In the process of synthesis for MTNI, 1-Methyl-4,5-dinitroimidazole (MDNI) was obtained, and its theory detonation velocity can reach 7 605 m/s, which is higher than that of TNT[18]. In recent years, a series of research of MDNI has been done by North University of China. Tanking imidazole as primary substance, MDNI was synthesized by SONG et al.[19]. MDNI was synthesized from nitration of 1-methylimidazole by CAO et al.[20]. In the research of LI et al., the single crystals of MDNI were prepared and its crystal structure was determined by a four-circle X-ray diffractmeter[21]. The thermal decomposition properties of MDNI were characterized by CHEN et al., and the results showed that its thermal stability was better than that of TNT[22]. In order to further realize and master the properties of MDNI, X-ray diffraction (XRD), differential scanning calorimeter (DSC) and impact sensitivity instrument

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were used to characterize its performance. In addition, the specific heat capacity, thermal kinetic parameters, thermal decomposition reaction rate constant and critical explosion temperature were calculated and analyzed.

1 Experiments

1.1 Materials

The materials MDNI and TNT were synthesized by North University of China.

1.2 Instrument and test conditions

An XRD, which is made by Dandong Haoyuan instrument Co., Ltd. of China, was used to characterize MDNI sample. The testing conditions were as follows: target material, Cu; tube voltage, 40 kV; tube current, 30 mA; start angle, 10°and end angle, 50°.

The DSC test was carried out with a DSC Q600 instrument, which is made by TA Co. Ltd of USA. In the test, each 1.0 mg sample was placed in a closed ceramic crucible. The samples were measured in triplicate with a temperature profile of room temperature to 375 ℃ with heating rates of 5, 15 and 20 K/min in a nitrogen atmosphere with a flow of 30 mL/min.

The ERL type 12 drop hammer apparatus was used for conducting the impact sensitivity test according to GJB-772A-97 standard method 601.3[23]. The testing conditions were as follows: drop weight, 2.500±0.002 kg; sample mass, 35±1 mg; and the relative humidity, 40%. The critical drop-height of 50% explosion probability (H_{50}) and standard deviation (S) were used to represent the test results.

2 Experiment results and discuss

2.1 XRD characterizations

MDNI sample was tested by X-ray diffraction. The pattern is shown in Fig. 1. Raw data of XRD pattern was analyzed by Jade software. The obtained data is displayed in Table 1. It can be seen from Fig. 1 and Table 1 that MDNI sample has good crystalline character and the distances of crystal faces are more or less the same. In addition, the main diffraction peaks are at 15.259°, 18.586°, 22.379°, 25.097°, 26.212° and 30.713°.

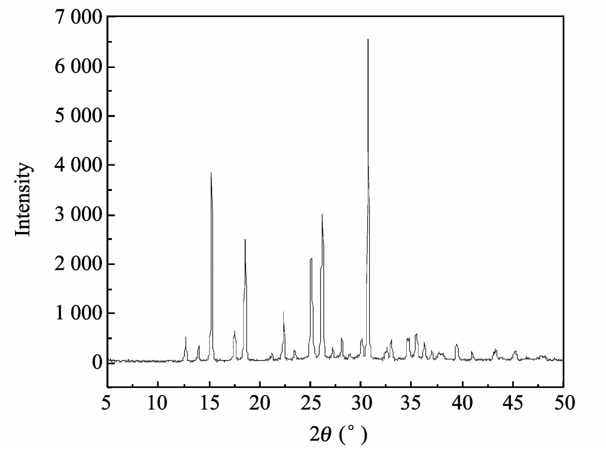

Fig. 1 XRD pattern of MDNI

Table 1 XRD data of MDNI

Peak No.	2θ(°)	d-value (Å)	Height	I (%)
1	12.708	6.960 3	498	7.7
2	13.977	6.330 9	294	4.6
3	15.259	5.801 7	3 764	58.4
4	17.565	5.044 9	582	9.0
5	18.586	4.770 1	2 428	37.6
6	21.253	4.177 1	128	2.0
7	22.379	3.969 4	958	14.9
8	23.449	3.790 7	183	2.8
9	25.097	3.545 3	2 008	31.1
10	26.212	3.397 0	2 899	44.9
11	27.210	3.274 6	216	3.3
12	28.104	3.172 4	398	6.2
13	28.929	3.083 9	92	1.4
14	30.108	2.965 7	388	6.0
15	30.713	2.908 7	6 450	100.0
16	32.600	2.744 5	251	3.9
17	32.998	2.712 3	384	6.0
18	34.755	2.579 1	367	5.7
19	35.484	2.527 8	451	7.0
20	36.313	2.471 9	306	4.7
21	37.010	2.427 0	184	2.9
22	37.756	2.380 7	163	2.5
23	38.004	2.365 7	132	2.0
24	39.472	2.281 1	313	4.9
25	40.998	2.199 6	153	2.4
26	43.251	2.090 1	219	3.4
27	43.878	2.061 7	48	0.7
28	45.287	2.000 7	184	2.9
29	46.339	1.957 7	57	0.9
30	47.783	1.901 9	83	1.3
31	48.168	1.887 6	79	1.2
32	49.115	1.853 4	39	0.6

2.2 DSC characterizations

Fig. 2 shows that the DSC curves of MDNI sample at heating rates of 5 ℃/min, 15 ℃/min and 20 ℃/min.

It can be seen from Fig. 2 that each DSC curve has an endothermic peak and an exothermic peak. The endothermic peak temperatures are 72.89 ℃, 74.01 ℃, 74.81 ℃ and the exothermic peak temperatures are 226.34 ℃, 252.39 ℃, 260.67 ℃ at heating rates of 5 ℃/min, 15 ℃/min and 20 ℃/min, respectively. The exothermic peak temperatures increase with the heating rate increased, but the endothermic peak temperatures change little. This may be explained by the fact that the melting point of MDNI sample is at about 74 ℃.

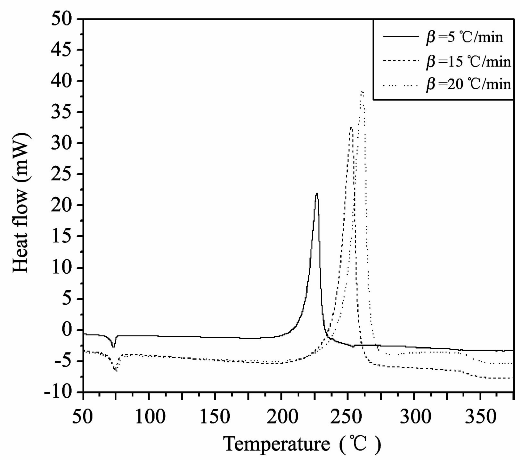

Fig. 2 DSC curves of MDNI

2.3 Specific heat capacity

The specific heat capacity of MDNI and TNT samples were tested by DSC direct method. DSC curves were selected within 40—100 ℃ with heating rate of 5 ℃/min. The results are shown in Fig. 3.

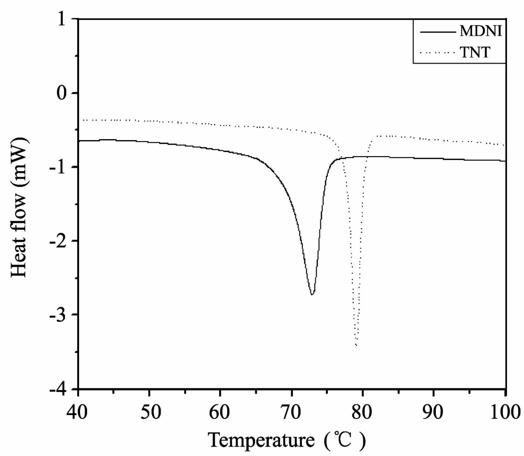

Fig. 3 DSC curves of explosive between 40 ℃ and 100 ℃

It can be seen from Fig. 3 that the phase of MDNI and TNT samples is solid and liquid when the temperatures are 60 ℃ and 90 ℃, respectively. At these two temperatures, the heat flow of MDNI is 0.776 2 mW and 0.883 0 mW, respectively and the heat flow of TNT is 0.432 4 mW and 0.626 7 mW, respectively. Based on Eq. (1), the specific heat capacity of MDNI is 9.314 4 J/(g • K) and 10.596 0 J/(g • K), respectively at heating rate of 5 ℃/min when the temperatures are 60 ℃ and 90 ℃, respectively. The specific heat capacity of TNT is 5.188 8 J/(g • K) and 7.520 4 J/(g • K), respectively in the same conditions. This phenomenon reveals that the specific heat capacity of explosive increases when it changes from solid phase to liquid.

$$C_p = \frac{HF}{m\beta}, \quad (1)$$

where HF is the heat flow in mW; m is the mass of explosive in kg; β is heating rate in K/min; C_p is the specific heat capacity of explosive in J/(g • K).

2.4 Thermal kinetic parameters

$$\ln(\beta/T_{pi}^2) = \ln(AR/E) - E/(RT_{pi}), \quad (2)$$

where E is apparent activation energy in kJ/mol; β is heating rate in K/min; T_{pi} is the peak temperature of decomposition at β in K; A is frequency factor in s^{-1}; and R is gas constant (8.314 J $mol^{-1}K^{-1}$).

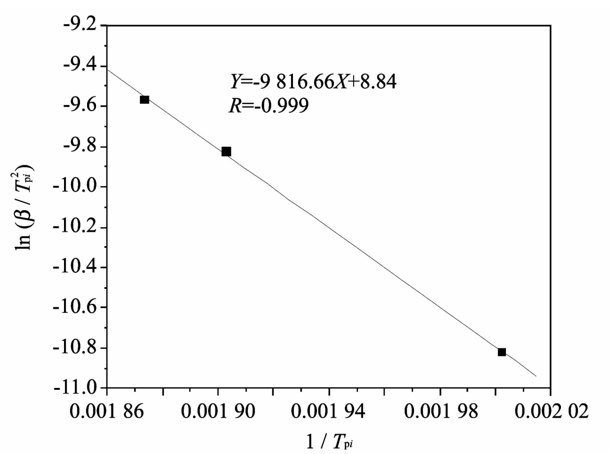

Fig. 4 Linear fitting of $\ln(\beta/T_{pi}^2)$ and $1/T_{pi}$, R is the linearly dependent coefficient

Based on the three peak temperatures at different heating rate, the Kissinger method (Eq. (2))[24] is used to acquire the thermal decomposition kinetic parameters of MDNI. When $\ln(\beta/T_{pi})$ is plotted against $1/T_{pi}$, a straight line is obtained and shown in Fig. 4. From the slope and the intercept, the apparent activation energy (E) and pre-exponential factor (A) of MDNI are calculated as 81.62 kJ/mol and 6.78×10^7 s^{-1}, respectively.

2.5 Thermal decomposition reaction rate constant

According to Arrhenius, the relationship between thermal decomposition reaction constant (k) and temperature of explosive can be determined by[25]

$$\log k = \log A - \frac{E}{2.3RT}. \qquad (3)$$

From Eq. (3), it can be found that $\log k$ has the linear function with $1/T$, the slope and intercept are equal to $E/2.3R$ and $\log A$, respectively. When the above apparent activation energy and pre-exponential factor were brought into Eq. (2), the linear relation between thermal decomposition reaction constant (k) and temperature is $\log k = 7.83 - 4\,268.11/T$.

2.6 Critical explosion temperature

The critical explosion temperature (T_b), which is an important parameter required to insure safe storage and process operations involving explosions, propellants and pyrotechnics, can be calculated by[26-27].

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2, \quad i = 1, 2, 3, \qquad (4)$$

$$T_b = \frac{E - \sqrt{E^2 - 4RET_{p0}}}{2R}, \qquad (5)$$

where b and c are constants; β_i is the heating rate in K/min; T_{pi} is the peak temperature of decomposition at β_i in K; T_{p0} is the peak temperature when β_i is zero in K; E is the apparent activation energy in kJ/mol; A is the frequency factor in s^{-1}; T_b is the critical explosion temperature in K.

First of all, T_{p0} is calculated as 208.57 ℃ according to Eq. (4). Then T_{p0}, E and A are brought into Eq. (5), the critical explosion temperature is calculated as 234.86 ℃.

2.7 Impact sensitivity

The impact sensitivities of MDNI and TNT samples were tested and analyzed. The results were shown in Table 2.

Table 2 Impact sensitivity results of explosives

Samples	Impact sensitivity, H_{50} (cm)	Standard deviation, σ
MDNI	95.3	0.022
TNT	104.2	0.072

As is shown in Table 2, the drop height for impact initiation of MDNI is 95.3 cm, which is 8.9 cm lower than that of TNT. This result show that there is no significant difference between MDNI and TNT in terms of impact sensitivity.

3 Conclusion

MDNI sample has good crystalline character and the distances of crystal faces are more or less the same. The main diffraction peaks are at 15.259°, 18.586°, 22.379°, 25.097°, 26.212° and 30.713°. The melting point of MDNI is about 74 ℃. The specific heat capacity of MDNI is 9.314 4 J/(g·K) and 10.596 0 J/(g·K) when the temperature is 60 ℃ and 90 ℃, respectively. With the changes of exothermic peak temperatures at different heating rates, the apparent activation energy and pre-exponential factor of MDNI are calculated as 81.62 kJ/mol and 6.78×10^7, respectively. The relationship between thermal decomposition reaction rate constant of MDNI and temperature is $\log k = 7.83 - 4\,268.11/T$. The critical temperature of MDNI thermal explosion is 234.86 ℃. The drop height for impact initiation of MDNI is 95.3 cm, which is 8.9 cm lower than that of TNT. There is no significant difference between MDNI and TNT in terms of impact sensitivity.

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1-甲基-4,5-二硝基咪唑的性能与表征

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摘　要： 采用X射线衍射仪(XRD)、差示扫描量热仪(DSC)和撞击感度仪分别对1-甲基-4,5-二硝基咪唑(MDNI)的性能进行表征。并对MDNI样品的比热容、热动力学参数、热分解反应速率常数、临界爆炸温度和撞击特性落高进行计算和分析。结果表明，MDNI样品为晶体结构且结晶良好。MDNI的熔点在74 ℃左右，在60 ℃和90 ℃时的比热容分别为9.314 4 J/(g·K)和10.596 0 J/(g·K)。MDNI的表观活化能为81.62 kJ/mol，指前因子为6.78×10^{7}，热分解反应速率常数(k)与温度的关系为 $\log k=7.83-4268.11/T$，临界爆炸温度为234.86 ℃，特性落高 H_{50} 为95.3 cm。

关键词： 1-甲基-4,5-二硝基咪唑；XRD；热分解；动力学；撞击感度

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