THERMAL DECOMPOSITION CHARACTERISTICS OF 1,7-DIAZIDO-2,4,6-TRINITRAZAHEPTANE AND ITS APPLICATION IN PROPELLANTS

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Abstract

The thermal decomposition characteristics of 1,7-diazido-2,4,6-trinitrazaheptane (DATH) and multi-component systems containing DATH were studied by using DSC, TG and DTG techniques. Three $-NO_2$ groups in the DATH molecule break away first from the main chain when DATH is heated up to 200°C. Following this process, the azido groups and the residual molecule decompose rapidly to release a great deal of heat within a short time. In the multi-component systems, DATH undergoes a strong interaction with the binder of the double-base propellant and a weak interaction with RDX. The burning rates of the two propellants were determined by using a Crawford bomb. The results showed that the burning rate rises by about 19–66% when 23.5% DATH is substituted for RDX in a minimum smoke propellant. Meanwhile, the N_2 level in the combustion gases is enhanced, which is valuable for a reduction of the signal level of the solid propellant.

Keywords: burning rate, DATH, DSC, TG, thermal decomposition

Introduction

1,7-Diazido-2,4,6-trinitrazaheptane (DATH) is an energetic oxidizer of propellants. An understanding of its thermal behaviour as an oxidizer is very important. In the field of studies of its thermal decomposition behaviour, no research reports appear to be available. The American Air Force studied certain combustion properties of the straight-chain azido-nitramine and proved that DATH can be used in a minimum smoke propellant [1]. In addition, there have been numerous reports on the thermal decompositions and combustion properties of other azido-nitramines [2–5]. In a continuation of our studies on the thermal behaviour of azido-organic compounds, we now report results on thermal decomposition of DATH and in part the combustion properties of a propellant containing DATH.

Experimental

Materials

The purified DATH used was prepared in the Xi'an Modern Chemistry Research Institute. The three-component and four-component systems in Table 1 were prepared by mixing the various compounds in acetone. Two minimum smoke propellant strands with and without DATH, used to measure the burning rate, were prepared by a solventless extrusion technique.

Table 1 Compositions of multi-component systems (mass %)

Sample	NC	NG	RDX	DATH
1	33	33	33	–
2	33	33	–	33
3	33	33	22	11
4	33	33	11	22

Experimental

TG and DSC experiments were carried out on a model TA 2000 instrument. The operating conditions were as follows: sample mass, about 2.00 mg; heating rate, 10 K min^{-1}; reference sample, α-Al$_2$O$_3$; atmosphere, a flow rate of about 40 ml min^{-1} of N$_2$. The burning rates from 2 to 14 MPa were determined for the strands burnt in a Crawford bomb.

Results and discussion

Thermal decomposition of DATH

DSC and TG-DTG of DATH curves are shown in Figs 1 and 2. It is clearly seen from Fig. 1 that there is a weak endothermal peak at about 135°C. This is a melting peak and the peak temperature rises as the pressure increases. DATH begins to decompose and release a little heat at 180°C. When the temperature attains 200°C, the DSC curves display a strong exothermic peak. The peak temperature falls slightly as the pressure rises. The experimental value for the first mass loss, between 150 and 195°C in the TG curves, 41.64%, agrees reasonably well with the theoretical mass loss of 43.12%, corresponding to the loss of the –NO$_2$ groups from the DATH molecule. This fact indicates that this stage involves the scission of the N–NO$_2$ bonds to release NO$_2$. The second mass loss process is the scission of C–N$_3$ to –C≡N+N$_2$ and decomposition of the residual molecule. The mass loss is up to 54% in the second process. The reason for the strong DSC peak is that the scission of C–N$_3$ releases a great deal of thermal energy within a very short time. The heat can accelerate the decomposition.
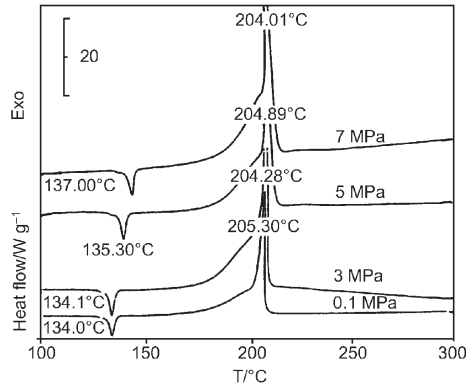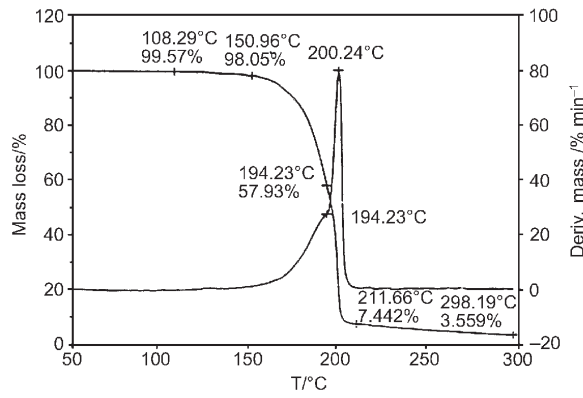
Fig. 1 DSC curves of DATH
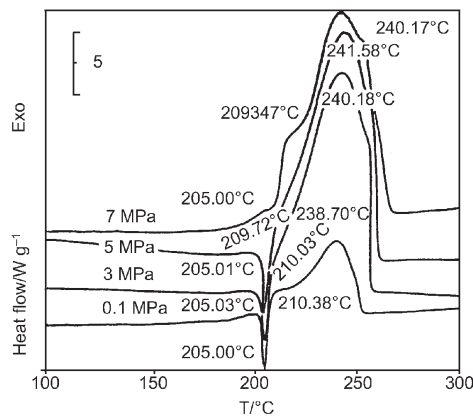

Fig. 2 TG-DTG curves of DATH

Fig. 3 DSC curves of sample 1

Thermal decomposition of three-component system

The DSC curves in Fig. 3 show that sample 1 has an endothermic peak at about 205°C up to 5 Mpa. The endothermic peak temperature is the melting point of pure RDX. The peak disappears above 7 MPa. The reason might be the strong reaction under high pressure and the release of heat of decomposition in excess of the melting heat of RDX. The binder then begins to decompose. However, the peak of (NC+NG) decomposition is almost covered by the exothermal peak of RDX decomposition at high pressure. The peak temperature is almost the same as that for pure RDX decomposition. In addition, there are two mass loss stages in the TG-DTG curves in Fig. 4. The first stage involves only a small mass loss. The material lost might be some small molecule. The second stage is the main mass loss process. It includes two parts: the first part is mainly the loss of (NC+NG) and the second that of RDX.
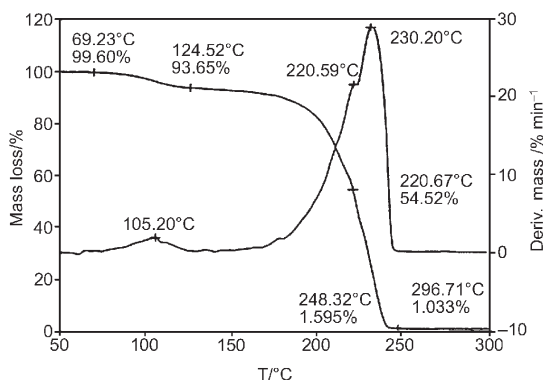

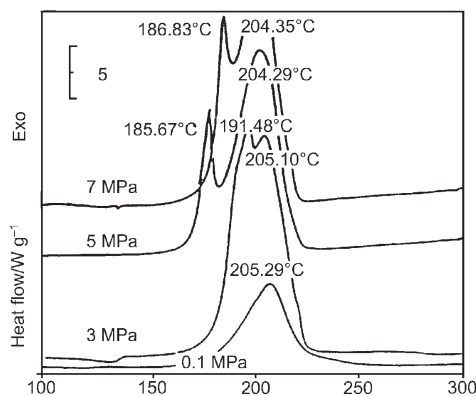**Fig. 4** TG-DTG curves of sample 1

Fig. 5 DSC curves of sample 2

The DSC and TG-DTG curves of sample 2 clearly differ from those of sample 1 (Figs 5 and 6). There is one decomposition peak only at 0.1 MPa. However, the de-
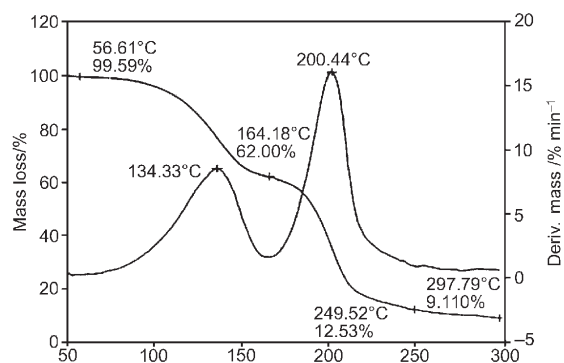
Fig. 6 TG-DTG curves of sample 2

composition peak changes into two peaks above 3 MPa. And the distance between the two peaks increases with increasing pressure. There are two mass loss stages in the TG-DTG curve in Fig. 6. The first stage is from 56 to 164°C. The mass loss is 36%. The data are totally accordant with the content of DATH in sample 2. This fact shows that the first mass loss process is DATH decomposition. Therefore, we consider that the two exothermal peaks of decomposition at high pressure correspond to DATH and (NC+NG) decomposition. There is a strong interaction between DATH and (NC+NG). The two peak temperatures are all lower than those for pure DATH and (NC+NG). The low peak temperature of decomposition is valuable to improve the burning rate of the propellant. The interaction between DATH and (NC+NG) is therefore very important.

Thermal decomposition of four-component system

There are two exothermal peaks in the DSC curves of samples 3 and 4 (Figs 7 and 8). At 0.1 MPa, however, there are three exothermal peaks for sample 3. The reason is that the released heat of the first exothermal process is less than the melting heat of RDX. However, the melting peak disappears above 3 MPa. This is because the decomposition reac-
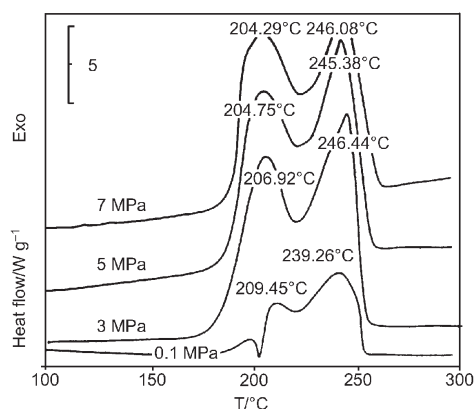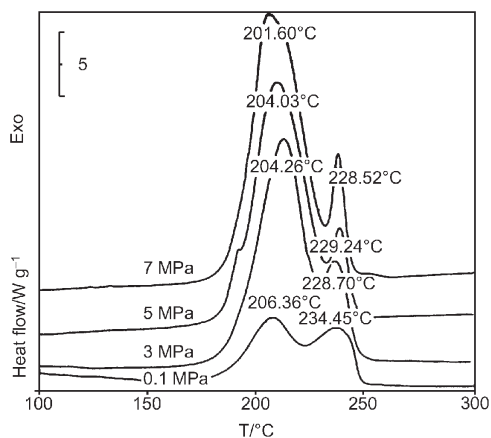

Fig. 7 DSC curves of sample 3
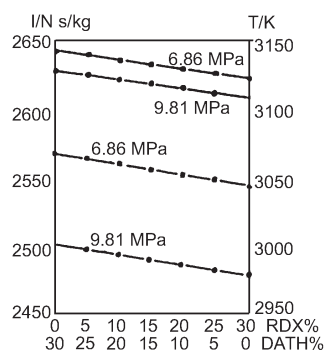
Fig. 8 DSC curves of sample 4

Fig. 9 Influence of DATH content on specific impulse (I_{sp}) and combustion temperature

tion becomes extremely rapid at high pressure. Additionally, the first and second peak temperatures of decomposition in the DSC curves all decrease with increasing pressure. The two peak temperatures of sample 4 are lower than those of sample 3 under the same conditions. We consider that the DATH content in sample 4 is more than that in sample 3, and accordingly we get the experimental results above. In general, DATH interacts strongly with (NC+NG) and weakly with RDX. DATH can accelerate the process of (NC+NG) decomposition, and (NC+NG) can also advance the process of DATH decomposition. The first mass loss is due to DATH decomposition. The second mass loss process relates to (NC+NG+RDX) decomposition.

Combustion characteristics

Theoretical evaluation

The enthalpy of formation of DATH is larger than that of RDX. According to theoretical evaluation, the theoretical specific impulse (I_{sp}) increases by 4 N s kg^{-1} after 15% DATH is used to replace RDX in a nitramine propellant. However, the theoretical
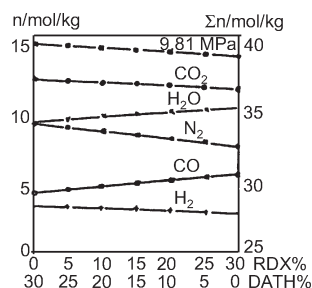
Fig. 10 Influence of DATH content on composition of combustion gases

specific impulse rises by 24 N s kg^{-1} when 30% DATH replaces RDX. The total amount of combustion gases rises by 0.95 mol kg^{-1}. However, the combustion temperature increases by only 21 K (Fig. 9). After DATH replacement for RDX, the quantities of CO_2, N_2 and H_2 in the combustion gases rise, and those of H_2O and CO decrease (Fig. 10). The increases in CO_2 and N_2 and the reduction in H_2O in the combustion gases are valuable in reducing the signal level of the solid propellants.

Burning rate determination

We used 23.5% DATH substituted for RDX in the minimum smoke propellant at the same energy level. The burning rates of two kinds of propellants were determined in a Crawford bomb at the same pressure. The burning rate curves are shown in Fig. 11.
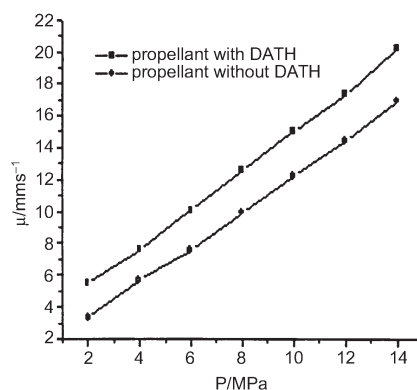

Fig. 11 Burning rate curves for propellants with and without DATH

Generally speaking, the burning rate for the propellant with DATH is larger than that for the propellant without DATH at the same pressure. The burning rate for the propellant with DATH rises by about 19–66%. The reason is that DATH has a large positive enthalpy of formation and releases a great quantity of gases when it decom-

poses. Therefore, DATH might have a good future for improvement of the burning rate of propellant. However, the pressure exponent of this kind of propellant is worse.

Conclusions

1. The process of DATH decomposition involves two stages: first, scission of the $-NO_2$ groups from the main chain to produce NO_2 when DATH is heated to 200°C, and second, decomposition of the $-N_3$ groups and the residual molecule; this process is accompanied by the release of a great deal of thermal energy within a short time.

2. DATH interacts strongly with (NC+NG) and the interaction is further improved on increase of the experimental pressure. However, the interaction between DATH and RDX is weak. The result of the strong interaction might be decreases in the peak temperatures of decomposition of DATH and (NC+NG). The low peak temperature is useful for improvement of the burning rate of the propellant.

3. The burning rate rises by about 19–66 when 23.5% DATH is substituted for RDX in the minimum smoke propellant at the same energy level. Meanwhile, the nitrogen content of the combustion gases increases, which is valuable in reducing the signature of solid propellants.

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