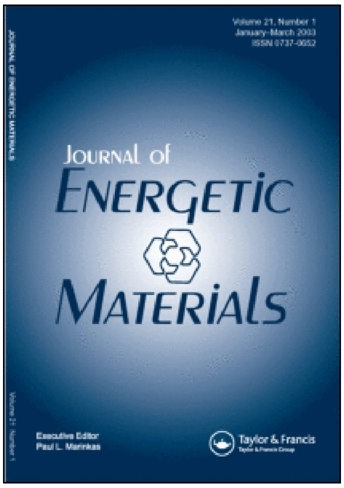

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THERMAL BEHAVIOUR OF 2,4,6,8,10,12-HEXANITRO-2,4,6,8,10,12-HEXAAZA-TRICYCLO $[7,3,0,0^{3,7}]$ DODECANE-5,11-DIONE

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Abstract

The thermal decomposition process of the title compound (HHTDD) under the conditions of vacuum and water vapour has been studied by using a highly sensitive Bourdon manometer. This process can be divided into induction period, acceleration period and deceleration period. All the decomposition curves exhibit the typical sigmoid shape. The relationship between the induction period (t_{in}) and the temperature (T) of the thermal decomposition of HHTDD in the temperature range 60 ~ 120℃ can be expressed by the following equations:

$$\ln t_{in} = 12586/T - 32.9503, \quad r = 0.9987 \tag{1}$$

and

$$\log t_{in} = 15.967 - 4.1854 \cdot 10^{-2} T, \quad r = 0.9988 \tag{2}$$

Acid and water are the principal factors affecting the stability of HHTDD. Water, especially has a devastating influence on HHTDD. Under linear temperature increase condition, the apparent activation energy of the thermal decomposition reaction of HHTDD is about 160 kJ mol^{-1}. The neutral hydrolytic reaction equation and ion dissociation process of HHTDD are proposed.

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1. Introduction

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaaza-tricyclo[7,3,0,$0^{3,7}$] dodecane-5,11-dione (HHTDD) is a new high explosive with zero oxygen balance. Its crystal density is 2.07 $g.cm^{-3}$. Theoretical detonation velocity of HHTDD is about 9700 $m.s^{-1}$. It was first synthesized in 1972 at our Institute. It has the potential for possible use as a high explosive from the point of view of the above-mentioned high performance. The aim of this work is to study the thermal behaviour under the conditions of vacuum and water vapour, the neutral hydrolytic reaction, the kinetic parameters and the degradation process of HHTDD by using a highly-sensitive Bourdon manometer, GC and chemical analysis method, DSC, and MS respectively.

2. Experimental

2.1 Materials

HHTDD with the acidity of 0.49, 0.43, 0.015 and 0.011% and the purified HHTDD used in this work are prepared at out Institute. The structure of the purified HHTDD is characterized by elemental analysis, molecular weight, IR spectrometry, mass spectrometry and NMR spectrometry. Its purity is more than 99.8%. And it is kept in a vacuum desiccator before use.

2.2 Experimental equipment and conditions:

The experiments of determining the thermal decomposition of HHTDD under isothermal conditions with a highly-sensitive Bourdon glass membrane manometer are carried out according to reported method [1]. The volume of reaction vessel of the manometer is about 15 ml for the complete decomposition and about 5 ml for the partial decomposition of HHTDD. Their loading densities are $1 \cdot 10^{-3}$ and $1 \cdot 10^{-1}$ g ml^{-1} respectively.

The experiments of the thermal decompostion of HHTDD under linear temperature increase conditions are carried out with a model CDR-1 thermal analyzer made in the Shanghai Balance Instrument Factory, using a Ni / Cr-Ni / Si thermocouple plate and working under static air conditions with six different heating rates ranging from 0.5 to 20℃ min^{-1} . Aluminum oxide is used as a reference material. Heating rate is calculated according to the actual rate of temperature rise from 50℃ to the temperature at the end of decomposition. The amount of sample used is about 0.5 mg.

The ion dissociation process of HHTDD is analyzed by using a MAT312/200 MS spectrometer (MAT Co., Germany). The conditions of MS are as follows: accelerating voltage of EI source, 3 kV; electron energy of EI source, 70 eV, emission current of EI source, 1 mA; vapourization temperature, 210℃.

3. Thermal decomposition of HHTDD

Under vacuum the complete decomposition of HHTDD at five temperature points from 155℃ to 195℃, and its partial decomposition at eight temperature points from 60℃ to 120℃ are carried out by using a highly–sensitive Bourdon glass membrane manometer.

The melting point of HHTDD used here is 205℃ (dec.). Its X–ray diffraction shows that there are two crystal forms, α and β. Form α is a white flashing crystalline substance, while Form β is a white powder. Because the stability of Form α is greater than that of Form β, HHTDD used in this study is of the former kind.

3.1 Complete decomposition of HHTDD

The V_H vs. t curves in Fig.1 represent the relationship between the standard volume of gas evolved (V_H) under standard condition (at 0℃ and 760 mm Hg) during the course of the sample decomposition and the time (t) of the complete thermal decomposition of HHTDD at 155℃, 165℃, 175℃, 185℃ and 195℃ with the loading density of the reactor m/V, as $1 \cdot 10^{-3}$ g ml^{-1} (m, sample weight; V, the volume of the reactor). All the decomposition curves exhibit the typical sigmoid shape. The maximum V_H, V_∞ is about 600ml.g^{-1}. The thermal decomposition process of HHTDD can be divided into three stages: induction period, acceleration period and deceleration period. The amounts decomposed within the induction period, the acceleration period and deceleration period are 1/8, 5/8, and 2/8 of the total amount decomposed respectively.

The curves of decomposition rate (dV_H / dt) vs. t are shown in Fig.2. The typical characteristic data of the thermal decomposition of HHTDD obtained from the V_H vs. t curves, the initial decomposition rate (W_0), the maximum decomposition rate (W_{max}), the induction period (t_{in}), the half decomposition period ($t_{1/2}$), the time to maximum decomposition rate (t_{max}), the initial rate constant (k_0), the maximum rate constant (k_{max}) and the average overlap coefficient (k_{dh}) are listed in Table 1. The relationships of the logarithm of the characteristic values in Table 1 versus the reciprocal of absolute temperature are shown in Fig.3. It can be seen from Fig.3 that under our conditions, the thermal decomposition process of HHTDD obeys the Arrhenius law. And the values of W_0, W_{max}, k_0, k_{max} and k_{hd} increase, whereas those of t_{in}, $t_{1/2}$ and t_{max} decrease, with the increase of thermal decomposition temperature of HHTDD. The values of the apparent activation energy (E) and the pre–exponential constant (A) obtained from Fig.3 are listed in Tables 2 and 3 respectively. Its deceleration period does not agree with the first order reaction law (see Fig. 4).

3.2 Partial decomposition of HHTDD

The curves of V_H vs. t and dV_H / dt vs. t of the partial thermal decomposition of HHTDD at 60℃, 65℃, 70℃, 80℃, 90℃, 100℃, 110℃, and 120℃ with the loading density of 0.1 $g.ml^{-1}$ are shown in Figs. 5 – 7 respectively. It can be seen from Fig.5 that all the standard volumes of gas evolved within the induction period (t_{in}) are about 1.25 $ml.g^{-1}$. If the gaseous products of the thermal decomposition of HHTDD reach the thermodynamic end–state, the maximum standard volume of gas evolved during the thermal decomposition process of HHTDD, V_∞, would be 670 $ml.g^{-1}$ in theory. At this time, their decomposition extent is 0.18%. The values of t_{in} corresponding to the value of 0.18% at different temperatures are listed in Table 4. The relationship between the values of t_{in} and the temperatures of thermal decomposition of HHTDD in the temperature range of 60~120 ℃ (shown in Table 4) can be expressed by the following equations

$$\ln t_{in} = 12586/T - 32.9503, \qquad r = 0.9987 \qquad (1)$$

and

$$\log t_{in} = 15.967 - 4.1854 \cdot 10^{-2}T, \qquad r = 0.9988 \qquad (2)$$

The values of the apparent activation energy, the pre–exponential constant and the safe lifetime of HHTDD at 20℃ obtained from eqn. 1 are 105 kJ.mol^{-1} , 10$^{14.3}$ (day)$^{-1}$ and about 55 years respectively.

4. The influence of acid on the thermal decomposition of HHTDD

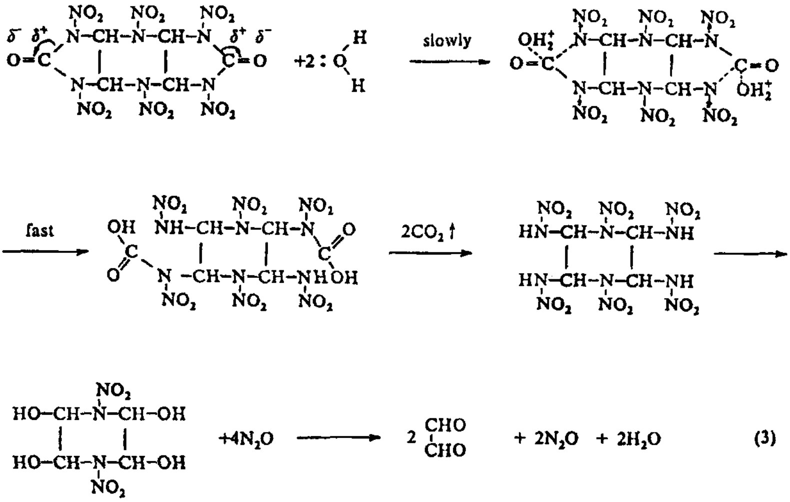
Acid has a great influence on the thermal stability of HHTDD. As shown in Table 5, if acidity is reduced by a factor of 1 / 5, the thermal stability will accordingly increase by 100%.

5. The influence of water vapour on the thermal stability of HHTDD.

HHTDD is extremely sensitive to water. The results (see Fig.8) of the thermal deocmposition of HHTDD in vacuum and in the presence of water vapour pressure of 24 mm Hg indicate that the decomposition rate of the later is about two times as great as the former and that the reaction of the later is strongly accelerated by water vapour.

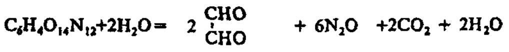
The hydrolytic reaction of HHTDD is zero order reaction in the temperature range of 35 – 55℃ . The hydrolytic rate constants at 35℃ , 45℃ and 55℃ are 1.85 • 10^{-5} , 9.59 • 10^{-5} , and 28.3 • 10^{-5} mol(day)$^{-1}$ respectively. The values of E and A of this reaction is 114.6 kJ.mol^{-1} and 10$^{14.8}$ (day)$^{-1}$ respectively. The linear correlation coefficient is 0.9950. The time required for a 1% mass–loss of HHTDD at a temperature of 18℃ and relative humidity of 66% is only 10 days.

The neutral hydrolytic products of 1 mol HHTDD in the temperature range 20–60℃ determined by using GC and chemical analysis method are 2 mol water, 5.8 mol nitrous oxide, 1.9 mol carbon dioxide and 1.9 mol acetic dialdehyde. On the basis of above–mentioned experiments and calculated results, the possible mechanisms and equation of the neutral hydrolytic reaction of HHTDD are deduced to be as follows:



(3)

and



$$C_6H_4O_{14}N_{12}+2H_2O = 2\begin{matrix}CHO\\ CHO\end{matrix} + 6N_2O + 2CO_2 + 2H_2O \qquad (4)$$

6. The apparent activation energy of the thermal decomposition of HHTDD under linear temperature increase condition

In order to obtain the apparent activation energy (E) of the thermal decomposition of HHTDD, a multiple heating method [2] was employed. From the original data in Table 6, the calculated value of E is determined to be 166 kJ mol^{-1}. The linear correlation coefficient is 0.9972. The values of E determined from the exothermic rate equation [3] by a single non–isothermal DSC curve obtained with a heating rate of 5℃.min^{-1} is 156 kJ mol^{-1}. These values of E are in fair agreement with the values of E of 157 (or 165) $kJ.mol^{-1}$ obtained from the relationship of log t_{max} (or k_{max}) versus 1 / T in Table 2. Therefore, the value of E of about 160 $kJ.mol^{-1}$ for the thermal decomposition of HHTDD is acceptable.

7. The ion dissociation process of HHTDD

The mass spectroscopy studies are carried out on a MAT–312 / 200 mass spectrometer. Its mass spectrum under the condition of low resolution (R = 1000) is shown in Fig.9. Under the condition of high resolution (R = 10000), the accurate mass and elemental composition of essential ions during the mass spectral fragmentation process of HHTDD are listed in Table 7. The relationship among the essential ions obtained by metastable scans is shown in Fig. 10. On the bases of the above–mentioned results the ion dissociation processes of HHTDD could be expressed by the scheme shown in Fig. 11.

8. Conclusions

(1) The thermal decomposition process of HHTDD can be divided into induction period, acceleration period and deceleration period. All the decomposition curves exhibit the typical sigmoid shape.

(2) The relationship between the induction period and the temperature of the thermal decomposition of HHTDD in the temperature range 60–120℃ can be expressed by the equations 1 and 2 shown in the Text. Its values of the apparent activation energy and the pre–exponential constant are 105 $kJ.mol^{-1}$ and $10^{14.3}$ $(day)^{-1}$ respectively.

(3) Acid and water vapour are the principal factors affecting the stability of HHTDD. Water vapour, especially, has a devastating influence on HHTDD.

(4) The mechanisms and equations of the neutral hydrolytic reaction of HHTDD can be expressed by the equations 3 and 4 shown in the Text.

(5) The value of the apparent energy of about 160 $kJ\ mol^{-1}$ for the thermal decomposition of HHTDD is acceptable.

9. References

1. MCRI–Q–AY–108–90 (China).
2. H.E.Kissinger, Anal. Chem. 29,1702(1957).
3. Hu Rongzu, Yang Zhengquan and Liang Yanjun, Thermochim. Acta, 123,135(1988).

Table 1

Characteristic data of the complete thermal decomposition of HHTDD at different temperatures

temp. ℃	W_0 ml/g.min	W_{max} ml/g.min	t_{in} min	$t_{1/2}$ min	t_{max} min	$k_0 \cdot 10^5$ s^{-1}	$k_{max} \cdot 10^5$ s^{-1}	k_{dh}
155	0.074	0.78	180	750	900	0.2042	0.6854	0.1693
165	0.19	2.54	90	306	376	0.5507	3.120	0.3910
175	0.37	7.26	46	127	145	0.9788	6.368	1.000
185	0.85	22.6	21	55	61	2.322	19.82	2.216
195	1.80	44.9	10.1	20.2	21.2	4.862	35.89	5.830

Table 2

Data of the apparent activation energy (E) of the complete thermal decomposition of HHTDD in the temperature range 155~195℃

Calculated method	E, kJ mol^{-1}
$\log W_0$ vs. $\frac{1}{T}$	133
$\log k_0$ vs. $\frac{1}{T}$	133
$\log t_{in}$ vs. $\frac{1}{T}$	121
$\log k_{dh}$ vs. $\frac{1}{T}$	148
$\log t_{1/2}$ vs. $\frac{1}{T}$	148
$\log t_{max}$ vs. $\frac{1}{T}$	157
$\log k_{max}$ vs. $\frac{1}{T}$	165
$\log W_{max}$ vs. $\frac{1}{T}$	177

Table 3

Data of the pre–exponential constant (A) of the thermal decomposition of HHTDD at different temperatures

temp. ℃	The value of A corresponding to k_0 $A \cdot 10^{-10}$, sec^{-1}	The value of A corresponding to k_{max} $A \cdot 10^{-17}$, sec^{-1}
155	3.5	2.7
165	4.2	3.9
175	2.9	2.7
185	3.5	3.0
195	3.4	5.2
155~195	ave. 3.5	ave. 3.5

Table 4

The induction period during the thermal decomposition of HHTDD at various temperatures

Temp. ℃	60	65	70	80	90	100	110	120
$t_{in(\alpha = 0.18\%)}$, days	115	71	40	13.4	5.2	2.56	0.94	0.32

Table 5

The influence of acid on the thermal stability of HHTDD

Acidity, %	Loss of weight at 100℃ for 8 days %
0.49	55.4
0.43	4.74
0.015	1.12
0.011	0.58

Table 6

The maximum peak temperature (T_m) of the thermal decomposition of HHTDD determined by the DSC curves at various heating rates (Φ)

Φ, deg.min^{-1}	T_m, K
0.5224	195
1.035	204
2.143	212
5.600	221
10.43	228
20.83	239

Table 7

The accurate mass and elemental composition of essential ions during the mass spectral fragmentaton process of HHTDD under the condition of high resolution (R = 10000)*

m / e	accurate mass		elemental
	experimental	theoretical	composition
124	124.0380	124.0385	$C_4H_4N_4O$
137	137.0464	137.0463	$C_5H_5N_4O$
171	171.0393	171.0392	$C_4H_5N_5O_3$
192	192.0397	192.0396	$C_6H_4N_6O_2$
193	193.0471	193.0474	$C_6H_5N_6O_2$
209	209.0425	209.0423	$C_6H_5N_6O_3$
210	210.0502	210.0513	$C_6H_6N_6O_3$
216	216.0246	216.0243	$C_4H_4N_6O_5$
240	240.0061	240.0058	$C_6H_6N_7O_4$
261	261.0095	261.0093	$C_4H_3N_7O_7$
284	284.0251	284.0254	$C_6H_4N_8O_6$
285	285.0332	285.0332	$C_6H_5N_8O_6$
307	307.0020	307.0023	$C_4H_3N_8O_9$
330	330.0184	330.0183	$C_6H_4N_9O_8$
334	334.0133	334.0132	$C_5H_4N_9O_9$
376	376.0112	376.0112	$C_6H_4N_{10}O_{10}$
422	422.0037	422.0041	$C_6H_4N_{11}O_{12}$
468	467.9966	467.9970	$C_6H_4N_{12}O_{14}$

* PFK is used as a standard sample.

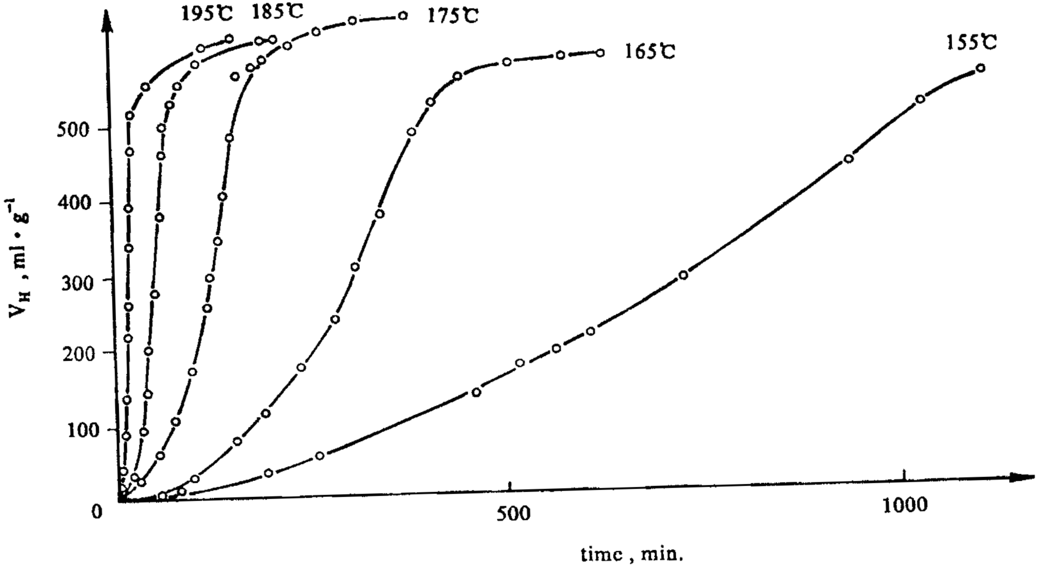


Fig. 1 The curves of change in gas formation with time during the thermal decomposition of HHTDD with the loading density of 1×10^{-3}g • ml^{-1}at various temperatures.

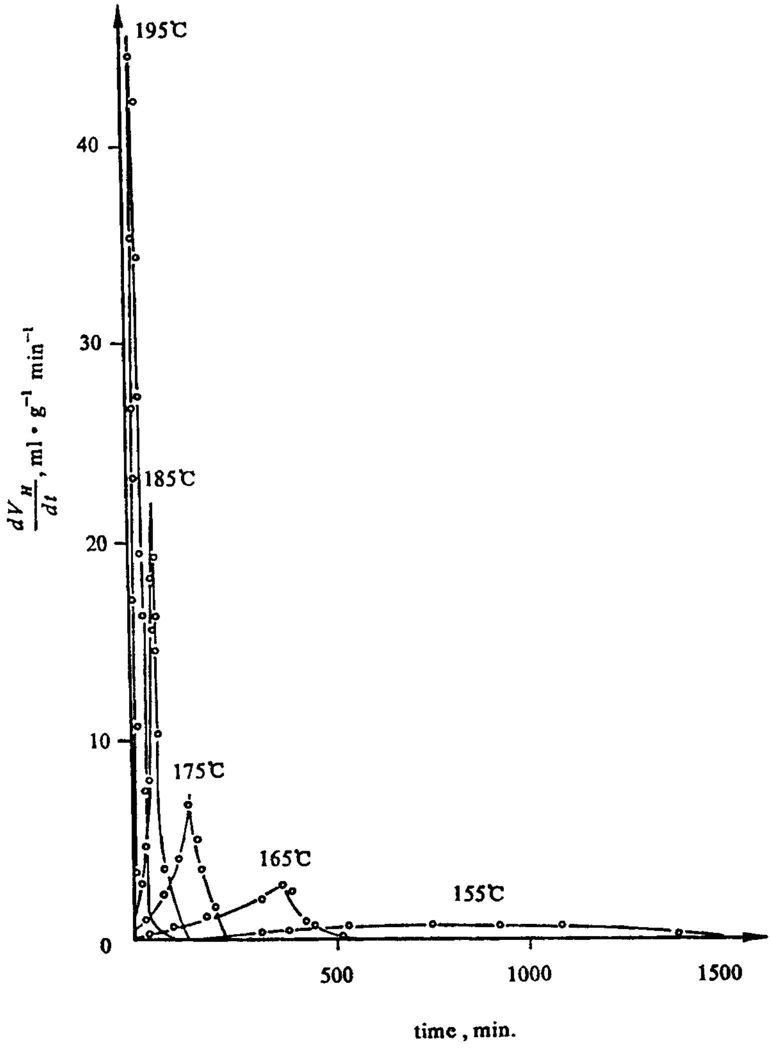


Fig. 2 The curves of change in rate with time during the thermal decomposition of HHTDD at various temperatures.

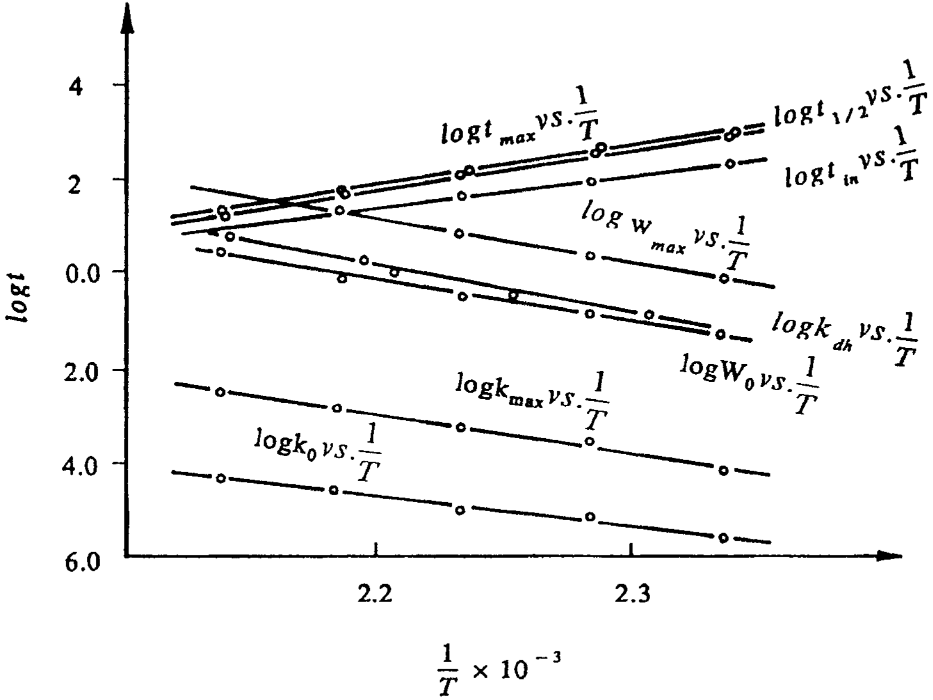


Fig. 3 logt as function of temperaturc.

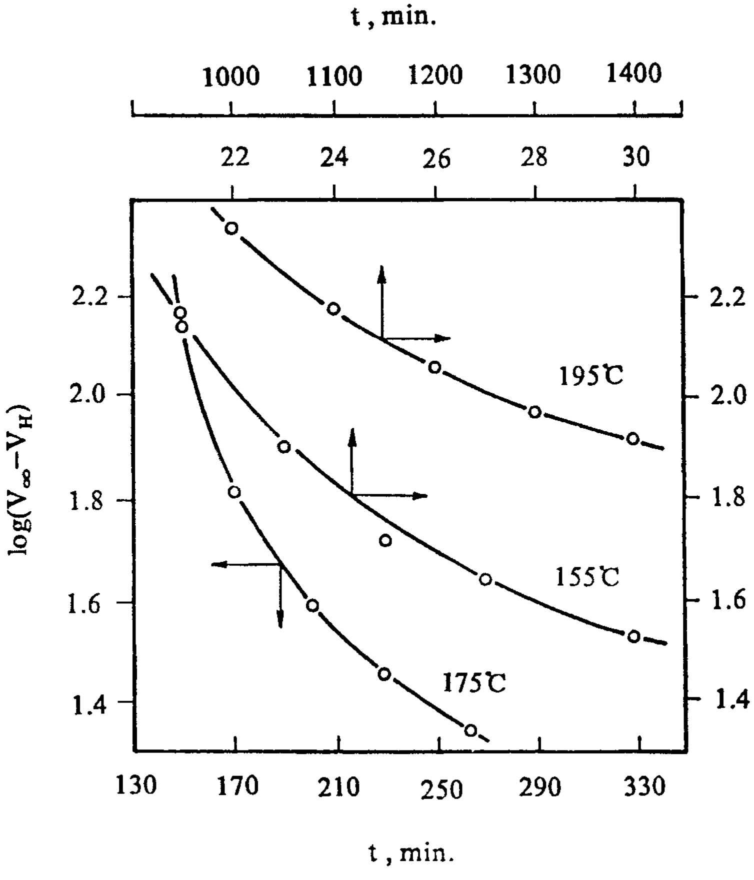


Fig. 4 Dependence of log($V_\infty-V_H$) on temperature .

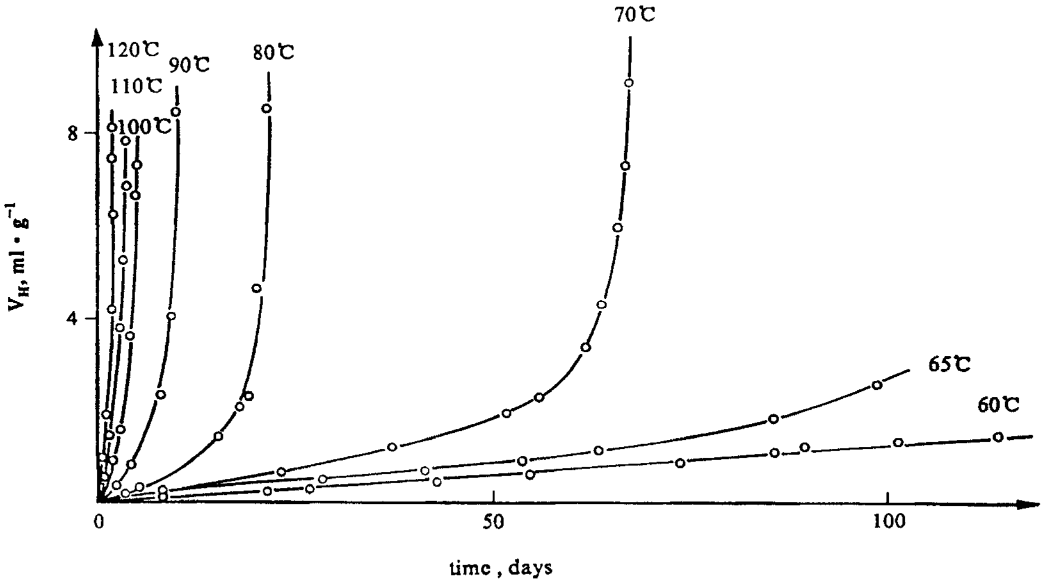


Fig. 5 The curves of change in gas formation with time during the thermal decomposition of HHTDD with the loading density of 1×10^{-1}g • ml^{-1} at various temperatures.

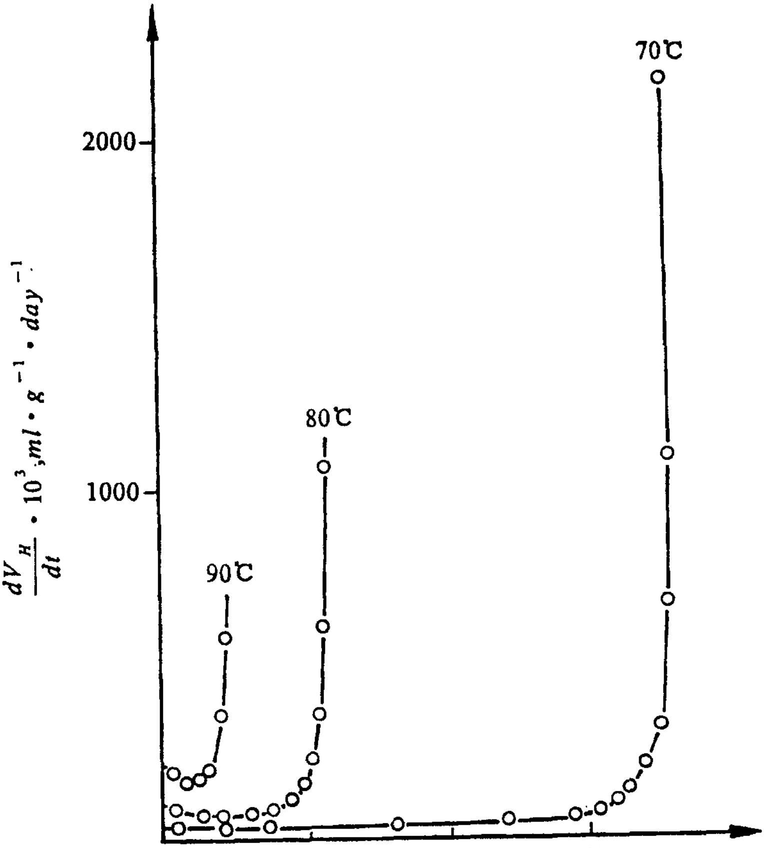


Fig. 6 The curves of change in rate with time during the thermal decomposition of HHTDD at various temperatures.

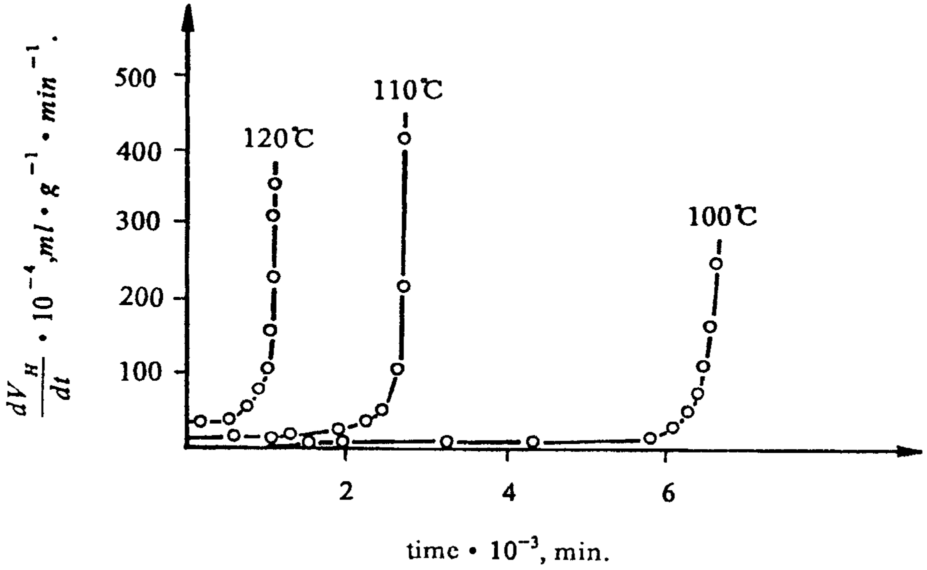


Fig. 7 The curves of change in rate with time during the thermal decomposition of HHTDD at various temperatures.

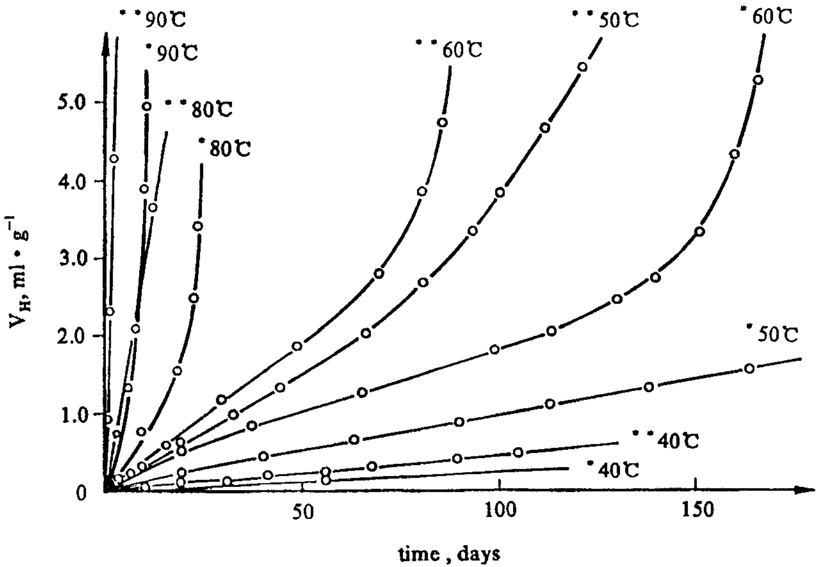


Fig. 8 The curves of change in gas formation with time during the thermal decomposition of HHTDD under the condition of vacuum (*) or water vapor of 24 mmHg(* *).

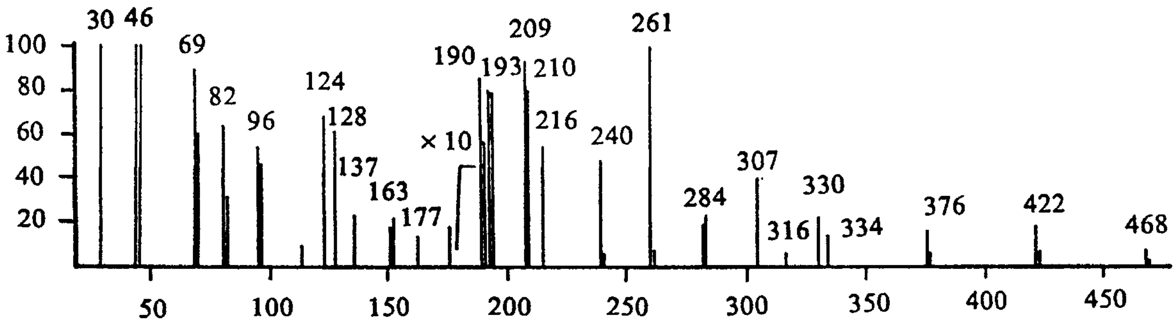


Fig. 9 Mass spectrum of HHTDD under the condition of low resolution (R = 1000)

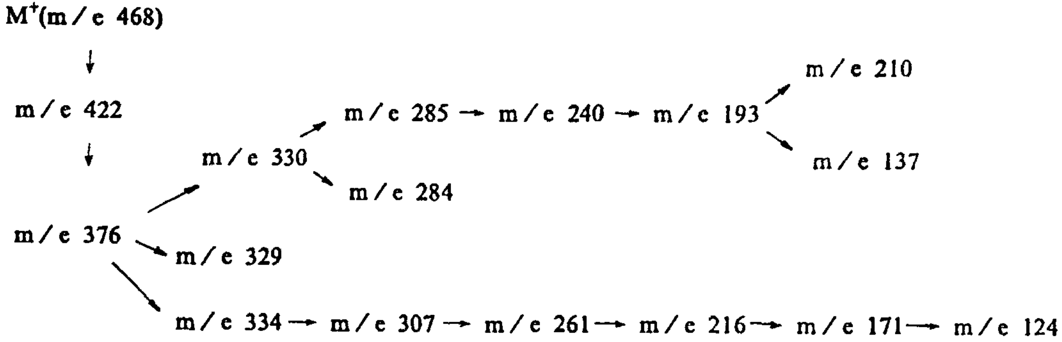


Fig. 10 The relationship among the essential ions obtained by metastable scans

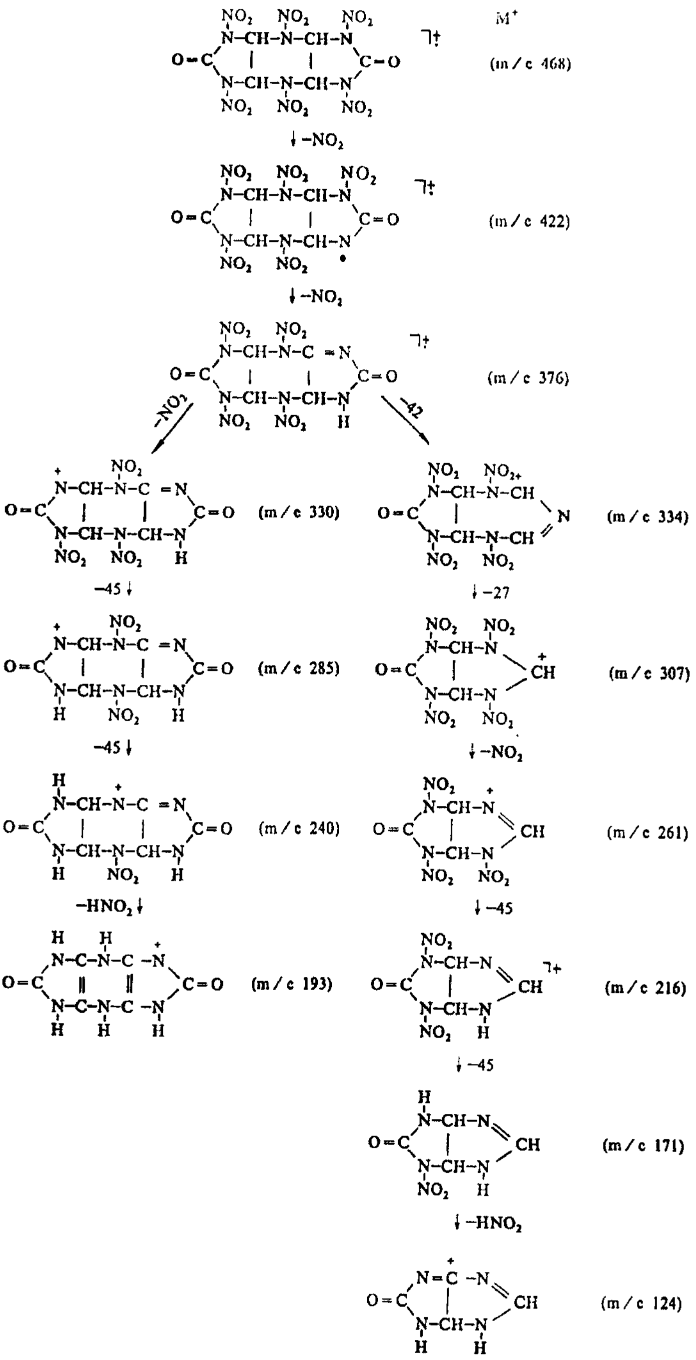


Fig. 11 The ion dissociation process of HHTDD