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MECHANISM OF THE INITIAL STAGE OF THE THERMAL DECOMPOSITION OF SOME CYCLOUREA NITRAMINES WITH *N*-TRINITROETHYL GROUPS

ZHANG HOUSHENG * and HU RONGZU *

Xian, Modern Chemistry Research Institute, Xian, Shaanxi (P.R. China)

YANG DESUO

Department of Chemistry, Baoji Teachers College, Baoji, Shaanxi (P.R. China)

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ABSTRACT

The mechanism of the initial stage of the thermal decomposition of nine cyclourea nitramines with *N*-trinitroethyl groups was studied using thermogravimetry, derivative thermogravimetry and differential scanning calorimetry, together with the chemical analysis of the gaseous products formed during this process. The solid intermediates were characterised and identified by infrared spectrometry. On the basis of the results obtained, a mechanism for the initial stages of the thermal decomposition of the above-mentioned compounds is proposed.

INTRODUCTION

Cyclourea nitramines with *N*-trinitroethyl groups have a greater density and a higher detonation velocity. Some of the compounds could be used as high explosives. The thermal stability, the stability of hydrolysis and the relationships between these properties and the electronic structure of this kind of compound have been studied in previous papers [1–3]. Their mechanisms, however, have rarely been reported. The aim of this work is to study the mechanism of the initial stage of the thermal decomposition of some cyclourea nitramines containing *N*-trinitroethyl groups by means of TG–DTG, DSC, IR, ultraviolet spectrometry (UV) and thin-layer chromatography (TLC).

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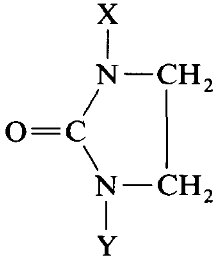
* Authors to whom correspondence should be addressed.

EXPERIMENTAL

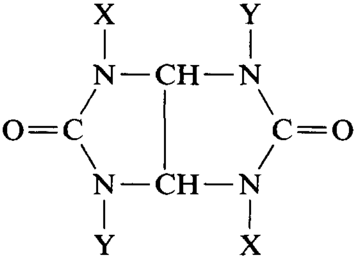
Materials

The following nine cyclourea nitramines with *N*-trinitroethyl groups used in this work were prepared and purified at our Institute.



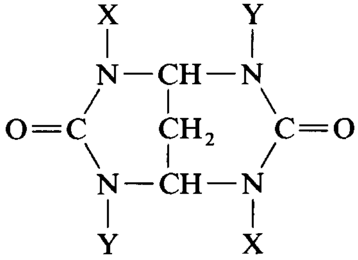
$X \equiv H, Y \equiv CH_2(NO_2)_3$, **I**

$X \equiv Y \equiv CH_2(NO_2)_3$, **II**



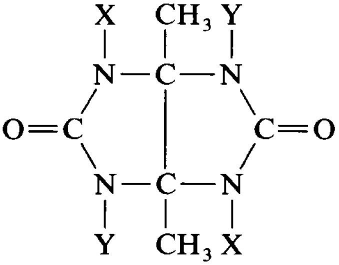
$X \equiv H, Y \equiv CH_2(NO_2)_3$, **III**

$X \equiv NO_2, Y \equiv CH_2(NO_2)_3$, **IV**



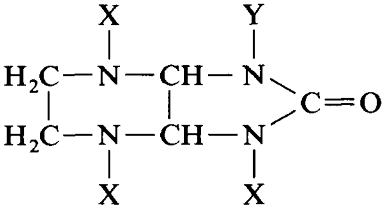
$X \equiv H, Y \equiv CH_2(NO_2)_3$, **V**

$X \equiv NO_2, Y \equiv CH_2(NO_2)_3$, **VI**



$X \equiv H, Y \equiv CH_2(NO_2)_3$, **VII**

$X \equiv NO_2, Y \equiv CH_2(NO_2)_3$, **VIII**



$X \equiv NO_2, Y \equiv CH_2(NO_2)_3$, **IX**

Compound **I** is a light yellow crystalline substance. Compounds **III** and **VI** are white powders. The others are all white and crystalline. Their structures were characterised by elemental analyses, molecular weight, IR, mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectrometry. Their purities were more than 99.5%. The compounds were kept in a vacuum desiccator before use.

EXPERIMENTAL EQUIPMENT AND CONDITIONS

TG–DTG curves were obtained using a Perkin–Elmer model TGS-2 thermobalance. The heating rate was 10 °C min^{-1}. The flow rate of N_2 gas was 40 ml min^{-1}. The amounts of samples used were about 0.6 mg. DSC experiments were carried out with a model CDR-1 thermal analyser made in the Shanghai Balance Instrument Factory, using a Ni/Cr–Ni/Si thermocouple plate and working under static air conditions with five different heating rates ranging from 1 to 23 °C min^{-1}. Aluminium oxide was used as a reference material in the DSC measurements. The heating rate was calculated according to the actual rising rate of temperature from 50 °C to the temperature at the end of the reaction.

IR spectra of solid intermediate products were recorded on a Perkin–Elmer model 180 IR spectrophotometer using the KBr disc technique. The gaseous intermediate products of the TG experiments were blown with high-purity N_2 gas and absorbed in an acetic acid solution of α-naphthylamine and *p*-aminobenzenearsonic acid, and in 95% ethyl alcohol respectively. The former solution, containing nitrogen dioxide, was purplish red in appearance. The latter solution obtained was tested by UV spectrophotometry and TLC. The characteristic UV absorption for the solution containing trinitromethane at 352 nm was observed, and the R_f value obtained by TLC analysis was 0.4.

RESULTS AND DISCUSSION

The gaseous intermediate products, the related data of the initial stage of the thermal decomposition and the kinetic parameters obtained by Kissinger's method [4] for the nine compounds are presented in Tables 1, 2 and 3 respectively.

TABLE 1

The gaseous intermediate products, NO_2 and $CH(NO_2)_3$, with temperature

Compound	The initial stage of thermal decomposition			
	T (°C)	Product	T (°C)	Product
I	132	NO_2	160	$CH(NO_2)_3$
II	160	NO_2	180	$CH(NO_2)_3$
III	195	NO_2	198	$CH(NO_2)_3$
IV	185	NO_2	200	–
V	170	NO_2	190	$CH(NO_2)_3$
VI	170	NO_2	190	–
VII	180	NO_2	203	$CH(NO_2)_3$
VIII	180	NO_2	204	–
IX	182	NO_2	190	–

TABLE 2

Data for the initial stage of the thermal decomposition of compounds **I–IX**

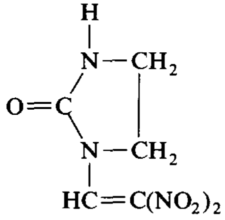
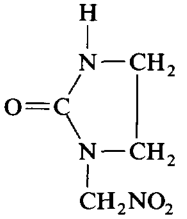
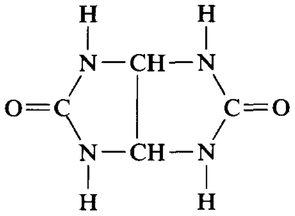
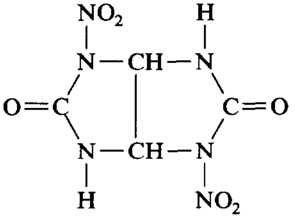
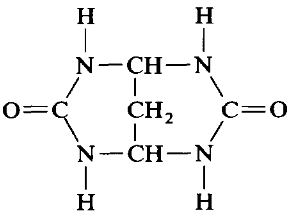
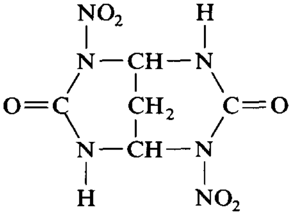
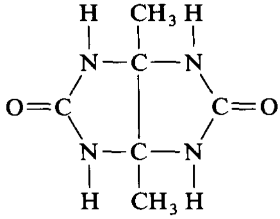
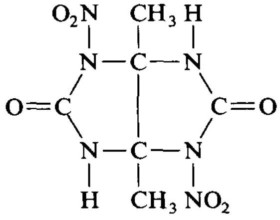
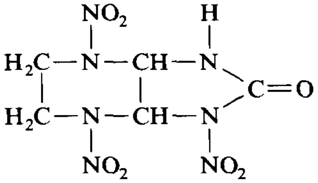
Decomposition stage	Temperature range (°C)		Weight loss (%)	
	TG	DTG	Obs.	Calc.
I ——→ 	110–156	110–129–156	18.5	18.9
II ——→ 	183–222	183–203–222	64.5	64.8
III ——→ 	155–272	155–216–272	60.3	69.6
IV ——→ 	180–231	180–210–231	53	58
V ——→ 	172–240	172–208–240	62.5	67.6
VI ——→ 	159–206	159–204–206	59.4	57.0

TABLE 2 (continued)

Decomposition stage	Temperature range (° C)		Weight loss (%)	
	TG	DTG	Obs.	Calc.
VII ——→ 	172-235	172-218-235	66	66
VIII ——→ 	170-240	170-218-240	56	55.7
IX ——→ 	188-218	188-213-218	39	37

The IR spectra of the solid intermediates, the TG–DTG and DSC curves are shown in Figs. 1 and 2, 3–7 and 8 respectively.

As shown in Table 1, nitrogen dioxide gas was liberated at the beginning of the decomposition of each compound. The compounds containing *N*-trinitroethyl with only one cyclourea or with bicyclourea and N–H groups produce trinitromethane when the decomposition reaction continued to a certain extent.

The IR spectra obtained for the intermediate products of the initial decomposition stage for different cyclourea nitramines containing *N*-trinitroethyl groups are similar, see Figs. 1 and 2. In Figs. 1 and 2, it can be observed that the intensity of the characteristic absorption peaks of trinitromethyl decreases as the temperature of the thermal decomposition increases. By the end of the exothermic first stage, the characteristic absorption peaks of trinitromethyl at 1600 cm^{-1} for compound **I**, at 1600 and 1300 cm^{-1} for compounds **II**, **III**, **VII** and **VIII**, at 1610 and 1300 cm^{-1} for compound **IV**, at 1625, 1580 and 1305 cm^{-1} for compound **V**, at 1620 and 1300 cm^{-1} for compound **VI** and at 1600 and 1305 cm^{-1} for compound **IX** have almost disappeared. However the characteristic absorption peaks of the –NH group for compounds **I** (at ~ 3300 cm^{-1}), **VII** (at 3240 cm^{-1}) and **IX**

TABLE 3

Calculated values of the kinetic parameters for the first-stage exothermic decomposition for compounds **I–IX**

Compound	ϕ [a]	T_m [b] (°C)	E (kJ mol^{-1})	log A (s^{-1})	r [c]
I	1.035	143.5	122.2	12.5	0.9922
	2.169	149.8			
	5.542	158.5			
	11.19	170.5			
	22.25	179.8			
II	1.139	179.2	177.0	17.8	0.9979
	2.292	185.0			
	5.438	192.2			
	11.04	200.8			
	22.64	208.2			
III	1.094	196.2	175.7	16.8	0.9932
	2.094	200.2			
	5.583	212.2			
	11.00	221.0			
	20.20	224.8			
IV	1.208	191.0	207.1	20.7	0.9943
	2.080	193.0			
	5.417	204.0			
	11.15	209.2			
	22.38	215.2			
V	1.208	183.5	169.5	16.6	0.9919
	2.300	191.0			
	5.278	200.5			
	9.938	207.5			
	21.90	215.5			
VI	1.175	182.0	182.0	18.2	0.9949
	2.143	187.5			
	4.750	197.2			
	11.00	204.0			
	22.00	209.5			
VII	1.156	197.5	208.4	20.4	0.9967
	2.000	203.5			
	5.250	211.2			
	10.60	218.8			
	22.75	224.0			
VIII	1.906	203.5	209.2	20.5	0.9972
	5.188	211.5			
	11.13	217.2			
	23.00	225.2			

Table 3 (continued)

Compound	ϕ^a	T_m^b (°C)	E (kJ mol^{-1})	log A (s^{-1})	r^c
IX	1.042	193.5	212.6	21.1	0.9976
	2.083	201.0			
	5.556	204.0			
	10.69	214.2			
	21.25	220.0			

[a] ϕ, Heating rate (°C min^{-1}).

[b] T_m, Maximum peak temperature.

[c] r, Linear correlation coefficient.

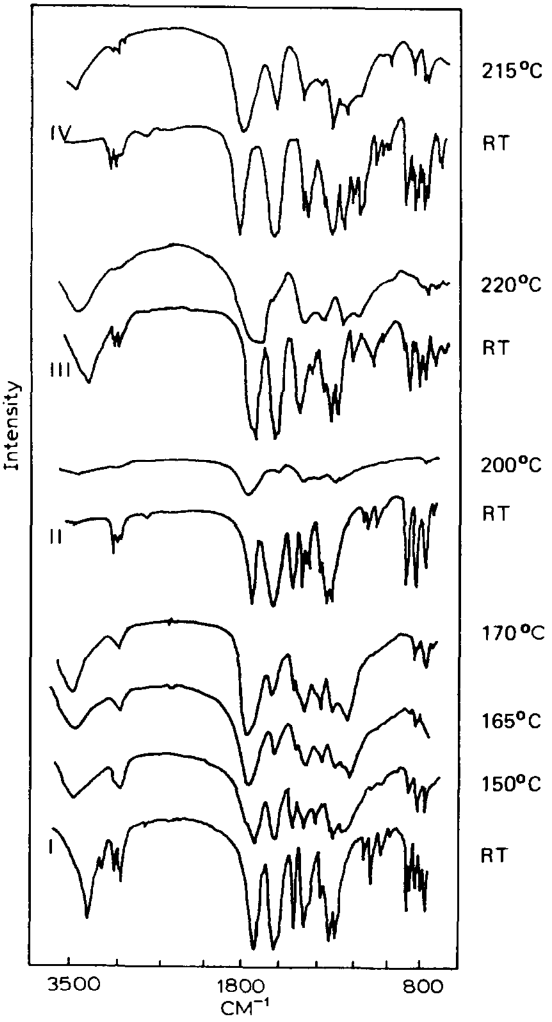


Fig. 1. IR spectra of compounds **I**–**IV** and their decomposition products (KBr pellet).

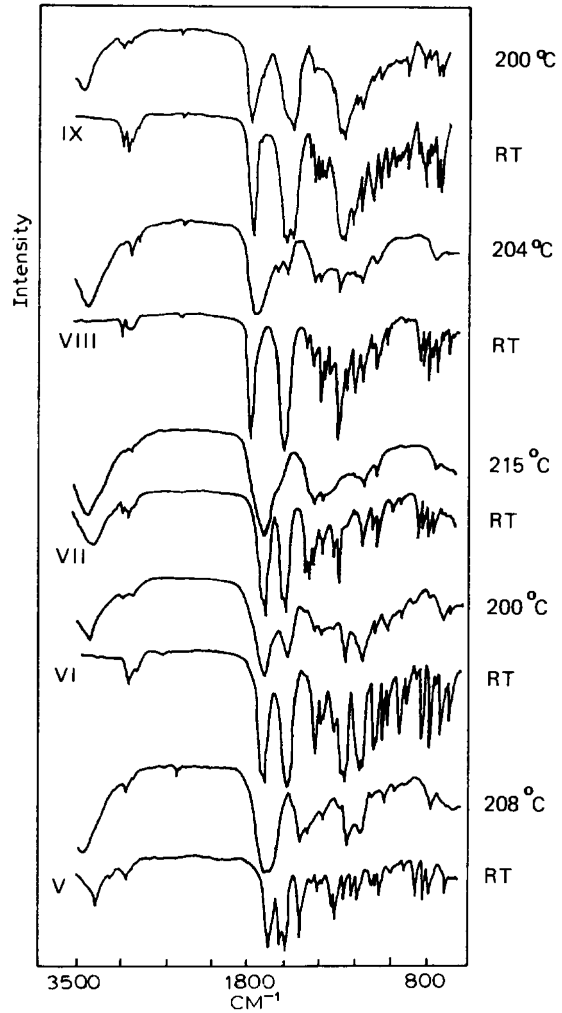


Fig. 2. IR spectra of compounds **V–IX** and their decomposition products (KBr pellet).

(at 3320 cm^{-1}), of the $>C-NO_2$ group for compound **II** (at ~ 1550, 1570 and 1360 cm^{-1}), of the $N-NO_2$ group for compounds **IV** (at 1585 and 1275 cm^{-1}), **VI** (at 1590 and 1280 cm^{-1}), **VIII** (at 1580 and 1270 cm^{-1}) and **IX** (at 1560, 1270 and 1300 cm^{-1}), of the $-CH$ group for compounds **III** (at 2860 and 1440 cm^{-1}), **IV** (at 3020, 1440 and 1380 cm^{-1}) and **IX**, of the $-CH_2$ group for compound **VI** (at 2920, 2860 and 1450 cm^{-1}), and of the $-CH_3$ group for compounds **VII** (at 2930, 2860 and 1435 cm^{-1}) and **VIII** (at 2930, 2860 and 1435 cm^{-1}) did not disappear. The characteristic absorption peaks of $>C=O$ widen. These observations showed that the parent ring of compounds **I–IX** did indeed exist.

A new IR characteristic peak appearing at 1620 cm^{-1} for the initial decomposition products of compound **I** showed that there was a C=C bond in the molecule of the resulting substance. The characteristic IR absorption

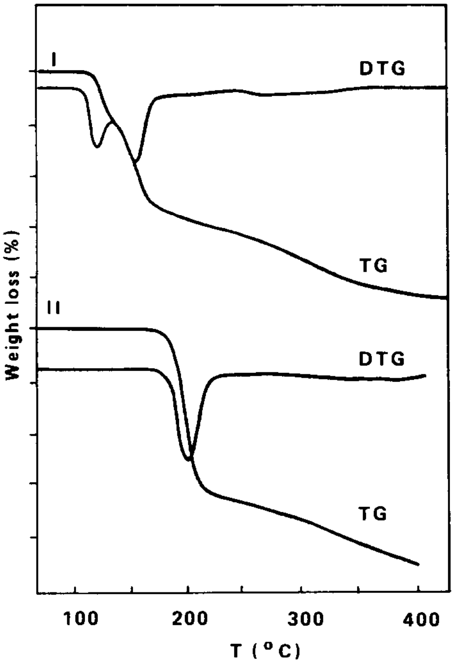


Fig. 3. TG–DTG curves of compounds **I** and **II**.

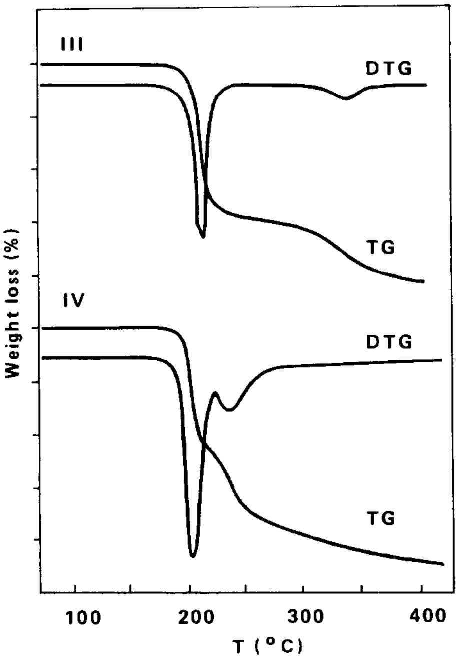


Fig. 4. TG–DTG curves of compounds **III** and **IV**.

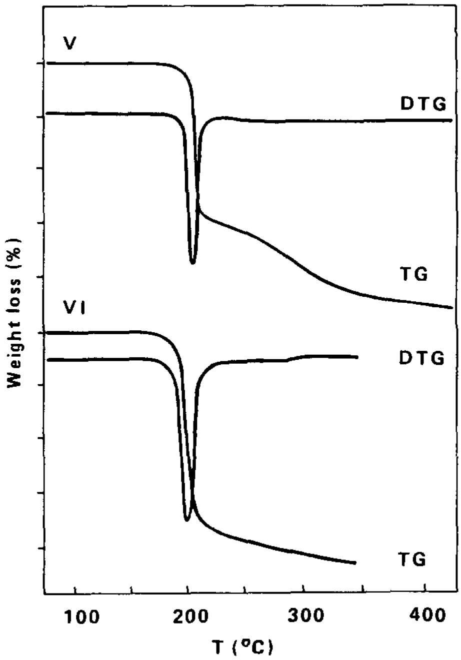


Fig. 5. TG–DTG curves of compounds **V** and **VI**.

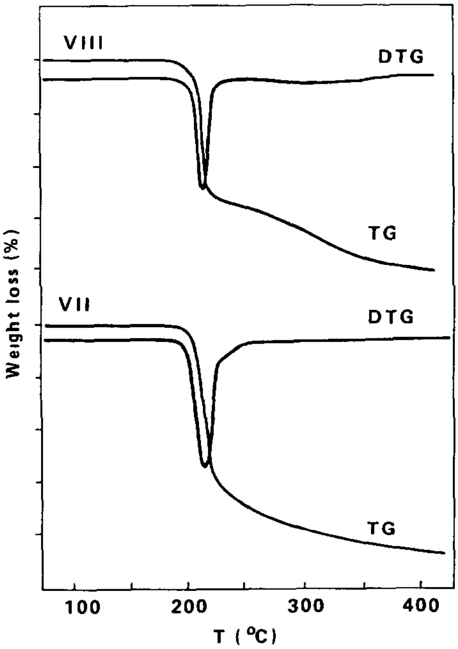


Fig. 6. TG–DTG curves of compounds **VII** and **VIII**.

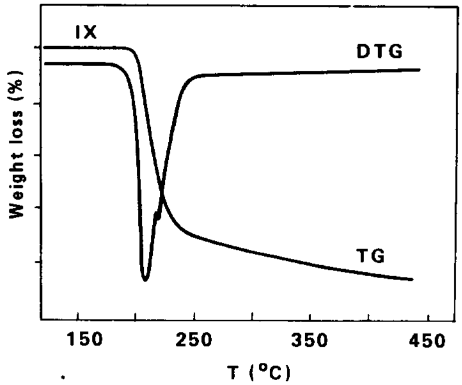


Fig. 7. TG–DTG curves of compound **IX**.

spectra of the products obtained at the end of the initial stage of the thermal decomposition for compounds **III** and **V** were in good agreement with data for glycoluril and data (at 3270, 3090, 1680, 1660, 1500, 1260 and 1170 cm^{-1}) for propanediurea respectively.

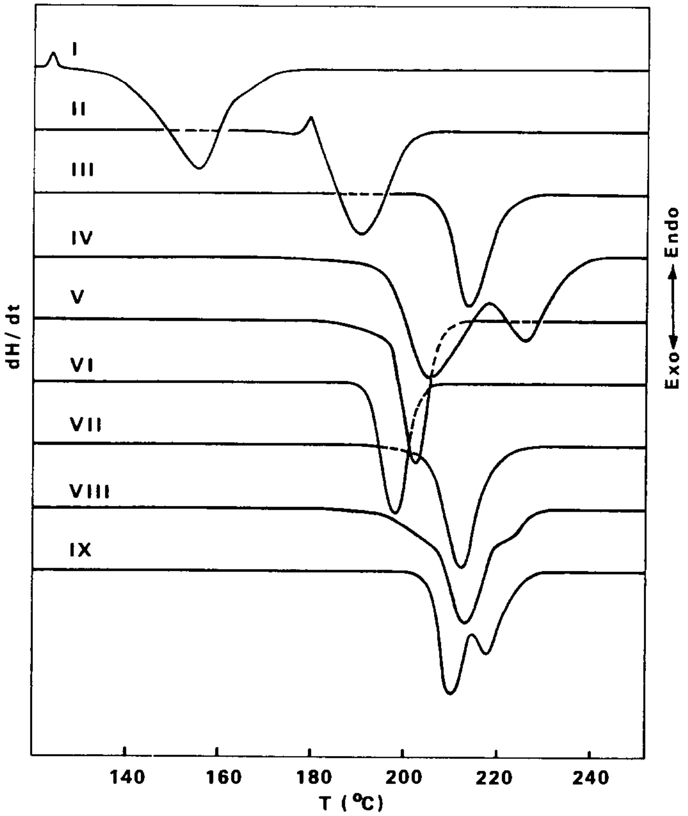


Fig. 8. DSC curves of compounds **I–IX** (heating rate 5 °C min^{-1}).

The weight losses on the TG curves of each compound were in agreement with the values calculated on the basis of the assumed initial decomposition stage (see Table 2).

In Table 3, we observed that the apparent activation energy (E) and pre-exponential constant (A) of the exothermic first stage decomposition for compound **I** were 122.2 kJ mol^{-1} and $10^{12.5}$ s^{-1} respectively. The values of E and A for the other compounds were 163–213 kJ mol^{-1} and $10^{18.2 \pm 2.5}$ s^{-1} respectively.

On the basis of above-mentioned experiments and calculated results, the mechanism of the initial decomposition of the nine compounds can be expressed as shown in Scheme 1.

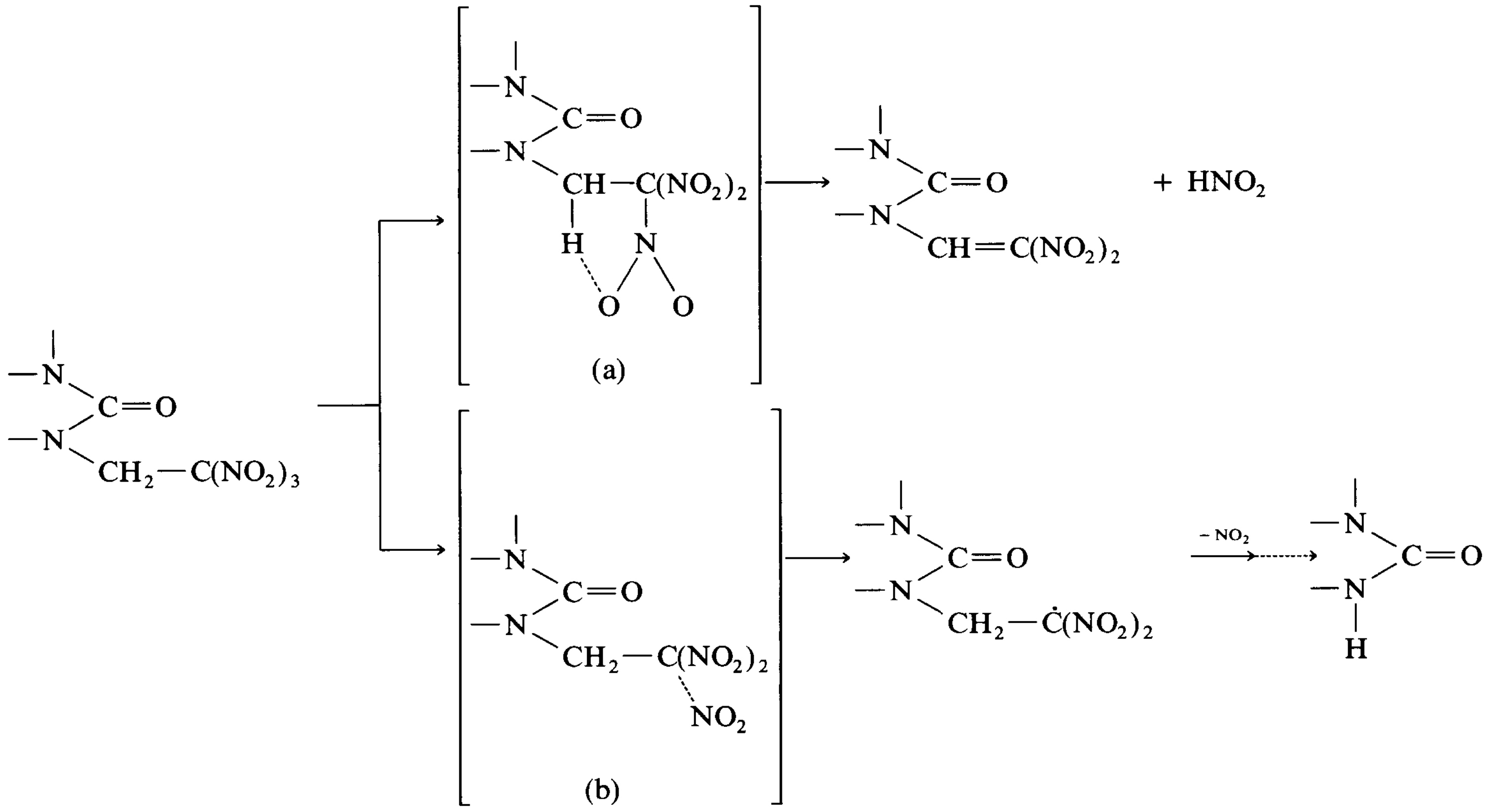
It is well known that the volume of a nitro group is large and that its polarity is very strong. If three nitro groups are crowded around one carbon atom, the strong repulsion between them decreases the strength of the $C-NO_2$ bond. This bond can be easily broken with heating.

The first step in the decomposition of these compounds is the rupture of the $C-NO_2$ bond in the trinitromethyl group and this is the rate-determining-step. Therefore, the activation energy of this step is close to the apparent activation energy.

Because the spatial surrounding of each trinitromethyl group is different in each compound, the two activated complexes, (a) and (b) as shown in Scheme 1, could be formed during decomposition. As for the activated complex (a), an H–O bond is formed, hence the activation energy of decomposition is lower. Compound **I** is a typical example and its E value is only 122.2 kJ/mol^{-1}. In the activated complex (b), a $C-NO_2$ bond was lengthened to a certain extent so that rupture of this bond was possible. The corresponding activation energy of this step was so high that it approached the dissociation energy of the $C-NO_2$ bond. Compounds **II–IX** have E values in the range 163–213 kJ mol^{-1}.

After the breaking of the $C-NO_2$ bond, the decomposition reaction continued with formation of some stable intermediate products. The main solid products are analogous to those formed by substituting the trinitroethyl group with a hydrogen atom. Other compounds, such as that produced by replacing only one nitro group within the trinitroethyl group with a hydrogen atom were also found. If the molecule contained the $N-NO_2$ group, this group was still present after decomposition even if the trinitroethyl was completely decomposed.

The decomposition mechanisms of these nine compounds were all similar but the thermal stabilities were different. From the data of the decomposition, such as the initial temperature and the activation energy, it could also be seen that the bicyclourea compounds are more stable than those with only one cyclourea, and that the thermal stabilities of the compounds are related to the symmetry of the molecular structure, the polarity, the effects of electricity and the spatial surroundings of the groups within the molecule.



Scheme 1.

CONCLUSIONS

(1) The mechanisms of the initial stages of the thermal decomposition for nine cyclourea nitramines containing *N*-trinitroethyl groups can be expressed by the schemes shown in Table 2 or in Scheme 1.

(2) The rupture of the $C-NO_2$ bond within the trinitromethyl group was easier than that the $N-NO_2$ bond in the parent ring in each cyclourea nitramine.

(3) The activation energy of 122.2 kJ mol^{-1} for the exothermic first-stage decomposition of compound **I** was lower than that found for the exothermic first-stage decomposition of compounds **II**–**IX** (163–213 kJ mol^{-1}).

(4) The thermal stabilities of those compounds containing bicyclourea are higher than those of compounds with only one cyclourea. The symmetry of the molecular structure, the polarity, the effects of electricity and the spatial surroundings of the groups within the molecule were some principal factors affecting the thermal stability of cyclourea nitramines.

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