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THERMAL STABILITY OF SOME FURAZANO-FUSED CYCLIC COMPOUNDS

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ABSTRACT

The thermal stability of 1,4,5,8-tetranitro-1,4,5,8-tetraazadifurazano[3,4-*c*:3′,4′-*h*]decalin (**I**) and its parent compound (**II**), 1,3,4-trinitro-imidazolinone[4,5-*b*]furazano[3,4-*e*]piperazine (**III**) and its parent compound (**IV**), 1,3,4,8-tetranitro-imidazolinone)[4,5-*b*]furazano[3,4-*e*]piperazine (**V**), 1,4,5,8-tetranitro-1,4,5,8-tetraazafurazano[3,4-*b*]decalin (**VI**) and 1,3,5-trinitro-1,3,5-triazafurazano[3,4-*f*]cycloheptane (**VII**) in static air has been studied by means of differential scanning calorimetry (DSC). Information is obtained on their thermal stability and decomposition.

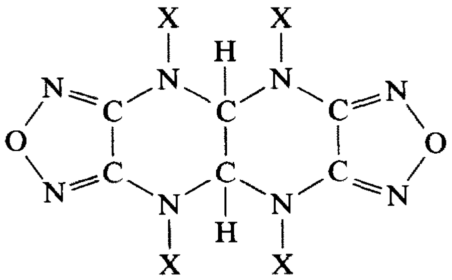
INTRODUCTION

Furazano-fused cyclic nitramines have a greater density and a higher detonation velocity compared with simpler nitramines. Some of the compounds can be used as high-explosives. The synthesis, thermal stability and the relationship between properties and structure of this kind of compound have been studied in previous papers [1,2]. However, the determination of thermal stability of furazano-fused cyclic compounds using DSC has not yet been reported. The aim of this work is to study their thermal stability by means of DSC.

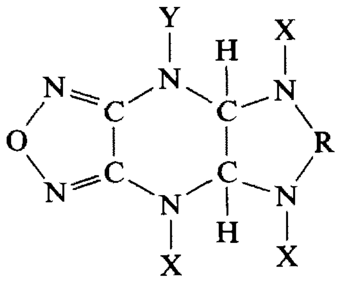
EXPERIMENTAL

Materials

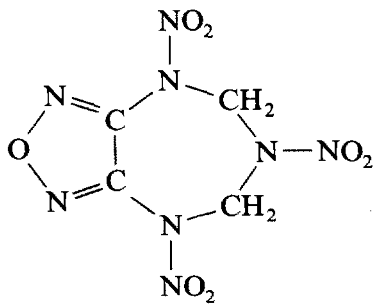
The following seven furazano-fused cyclic compounds used in this work were prepared and purified at our Institute.



$X = NO_2$, **I**
$X = H$, **II**



$X = NO_2$, $Y = H$, $R = C{=}O$, **III**
$X = Y = H$, $R = C{=}O$, **IV**
$X = Y = NO_2$, $R = CH_2$, **V**
$X = Y = NO_2$, $R = (CH_2)_2$, **VI**



VII

The structures of compounds **I–VII** are characterized by elemental analyses, molecular weight, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. Their purities are more than 99.0%. The compounds are kept in a vacuum desiccator before use.

EXPERIMENTAL EQUIPMENT AND CONDITIONS

DSC experiments 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 five different heating rates ranging from 0.5–20 °C min^{-1}. Aluminium oxide is used as a reference material. Heating rate is calculated according to the actual rate

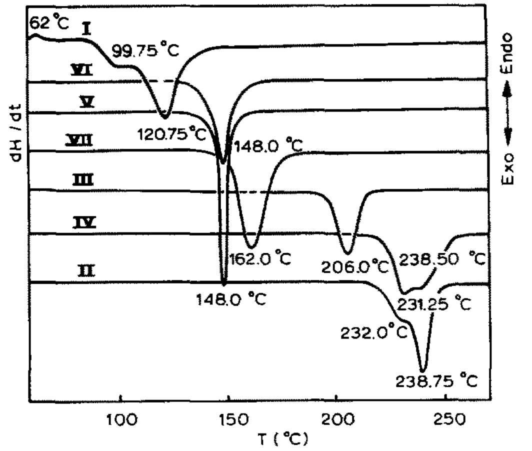


Fig. 1. DSC curves of compounds **I–VII** at a heating rate of 5 °C min^{-1}.

of temperature rise from 50 °C to the temperature at the end of decomposition. The amount of sample used is about 0.7 mg.

RESULTS AND DISCUSSION

DSC curves of compounds **I–VII** are shown in Fig. 1. The temperatures and kinetic parameters of their thermal decomposition are shown in Table 1. From Fig. 1 and Table 1 the following observations can be made.

(1) For compounds **I**, **II** and **IV** two exothermic peaks are obtained, whereas compounds **III** and **V–VII** each give only one exothermic peak.

TABLE 1

Temperatures and kinetic parameters of thermal decomposition of compounds **I–VII**

Compound	Decomposition temperature *		Kinetic parameters					
	T_{m1}	T_{m2}	E_1	E_2	log A_1	log A_2	r_1	r_2
I	99.75	120.75	79.6	275	8.91	34.6	0.9994	0.9987
II	232.0	238.75	183	158	16.9	13.8	0.9999	0.9982
III	206.0	–	232	–	23.4	–	0.9945	–
IV	231.25	238.50	156	130	13.9	11.0	0.9983	0.9984
V	148.0	–	270	–	31.8	–	0.9986	–
VI	148.0	–	218	–	25.1	–	0.9924	–
VII	162.0	–	283	–	32.1	–	0.9937	–

* Obtained upon heating (5 °C min^{-1}).

Key: T_m, maximum peak temperature of the DSC curve (°C); E, apparent activation energy obtained by Kissinger's method (kJ mol^{-1}); A, pre-exponential constant (s^{-1}); r, linear correlation coefficient.

(2) Compound **I** decomposes at 99.75 °C, whereas compound **II** decomposes at 232.0 °C. This shows that replacing X = H with X = NO_2 decreases the thermal stability.

(3) The substitution of only one nitro group for one hydrogen atom on the two amino groups conjugated with the furazano group (compare compound **III** with compound **IV**) decreases thermal stability.

(4) The substitution of nitro groups for hydrogen atoms on both the two amino groups conjugated with the furazano group further decreases the thermal stability (compare compound **IV** with compounds **V** and **VI**).

(5) The value of the apparent activation energy of thermal decomposition of compound **V** is greater than that of thermal decomposition of compound **VI** in the same temperature range. This shows that replacing ethyl with methyl increases thermal stability (compare compound **V** with compound **VI**).

(6) For compounds **III–VI**, the thermal stability of compounds **III**, **V** and **VI** is poorer than that of compound **IV**. This indicates that the hydrogen atom on the amino group can increase the stability of the furazano group.

(7) The results of the above-mentioned observations (3)–(6) indicate that the relative thermal stability of compounds **III–VI** decreases in the order **IV** > **III** > **V** > **VI**.

(8) Because two hydrogen atoms on the amino groups conjugated with the furazano-ring have been substituted by two nitro groups, the stability of compound **VII** is poorer than that of compounds **II**, **III** and **IV**.

In conclusion, the results indicate that the relative thermal stability of compounds **I–VII** decreases in the order **II** > **IV** > **III** > **VII** > **V** > **VI** > **I**. The thermal stability of these compounds is closely related to the substituents on the amino groups conjugated with the furazano group. Compound **III** has the potential for possible use as a high explosive from the point of view of its thermal stability.

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