Thermochimica Acta, 171 (1990) 35–38
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION MECHANISM OF 2,6,8,12-TETRANITRO-4,10-BIS(β,β,β-TRINITROETHYL)-2,4,6,8,10,12-HEXAAZATRICYCLO[7,3,0,$0^{3,7}$]-DODECANE-5,11-DIONE

HU RONGZU, ZHANG HOUSHENG, WU CHENGYUN, LIANG YANJUN, YANG DESUO, WANG YUAN, WANG JINSHENG and QI ZHUCHAI

Xian Modern Chemistry Research Institute, Xian, Shaanxi (People's Republic of China)

(Received 7 February 1990; in final form 9 April 1990)

ABSTRACT

Under non-isothermal conditions, the thermal behaviour of the title compound (TBHTDD) has been studied using TG–DTG and DSC. IR spectroscopy is used for the characterization of intermediate products. The thermal decomposition mechanism of TBHTDD is proposed.

INTRODUCTION

The title compound, TBHTDD, has a high crystal density and a high detonation velocity and it can be used as a high-explosive. Its thermal behaviour has never been reported. This paper describes the thermal behaviour of TBHTDD as studied by TG–DTG and DSC under non-isothermal conditions. The characterization of intermediate products formed during thermal decomposition was carried out on an IR spectrophotometer. This is quite useful in the study of thermal changes at high temperature and in the evaluation of thermal stability.

EXPERIMENTAL

The purified TBHTDD used was prepared in our Institute. The TG–DTG curve was obtained using a Perkin–Elmer model TGS-2 thermobalance. The heating rate was 2.5 ° C min^{-1} and the flow rate of N_2 gas was 40 ml min^{-1}. 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 at five rates in the range 1–20 ° C min^{-1}. Alumina was used as reference material in the DSC measurements. IR spectra of the solid intermediate products were recorded in KBr pellets using a Perkin–Elmer model 180 IR spectrophotometer.

0040-6031/90/$03.50

RESULTS AND DISCUSSION

The TG–DTG and DSC curves for TBHTDD are shown in Fig. 1. The DSC curve of Fig. 1 shows that there were three exothermic effects at temperatures higher than 120 °C. In Table 1 the initial and final temperatures of the thermal decomposition processes and the weight losses observed between these temperatures in the TG curve are given. The appearance of several peaks in the DSC curve suggests that this thermal decomposition process occurs in different steps. The IR spectra of some intermediate products of the thermal decomposition are shown in Fig. 2. The IR spectra of these intermediate products are completely different from that of the original sample at room temperature.

The thermal decomposition process of TBHTDD can be divided into four stages (Fig. 1). In the first stage, between 120 ° and 212 °C, a weight loss is observed corresponding to the loss of the two trinitroethyl groups attached to the nitrogen atoms adjacent to the carbonyl groups to obtain 2,6,8,12-tetranitro-2,4,6,8,10,12-hexaazatricyclo(7,3,0,$0^{3,7}$)dodecane-5,11-dione (THTDD). IR spectra (Fig. 2) of the products obtained at 212 °C showed that the characteristic absorption peaks for the trinitroethyl group at 1605 and 1305 cm^{-1} had disappeared. Comparison between Figs. 3 and 4 showed that all

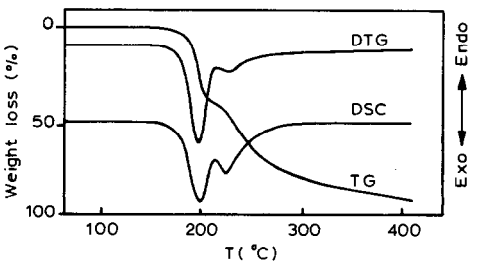

Fig. 1. DSC and TG–DTG curves for TBHTDD.

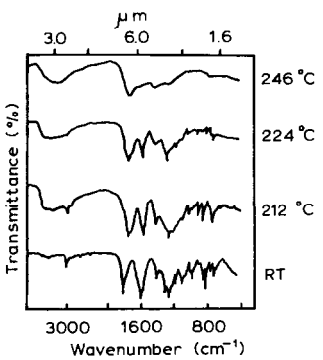

Fig. 2. IR spectra of TBHTDD and its decomposition products at different temperatures.

TABLE 1

Weight losses and corresponding temperatures for TBHTDD

T (°C)	TBHTDD weight loss (%)	
	Exp.	Theory
120–212	47.1	46.3
212–224	12.4	12.8
224–246	13.2	13.3
246–410	18.8	–

the peaks in Fig. 3 are maintained in Fig. 4. The ^{1}H peaks at 6.68, 7.90 and 9.10 ppm in Fig. 4 are attributable to THTDD. Peaks A, B, C, D and E were recognized as being due to THTDD. There were six new small peaks, F, G, H, I, J and K, in Fig. 4. It was assumed that small quantities of other intermediate products were formed. The formation of THTDD from the original sample would be accomplished with a theoretical weight loss of 46.3%. This was in agreement with the experimental value of 47.1%.

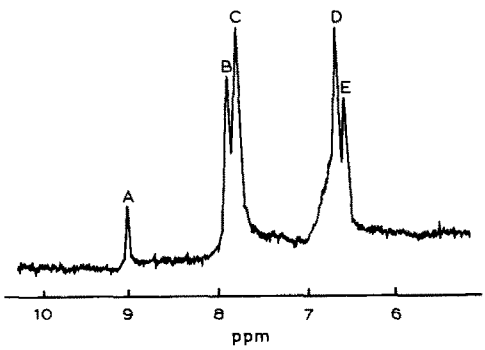

Fig. 3. ^{1}H spectrum of THTDD.

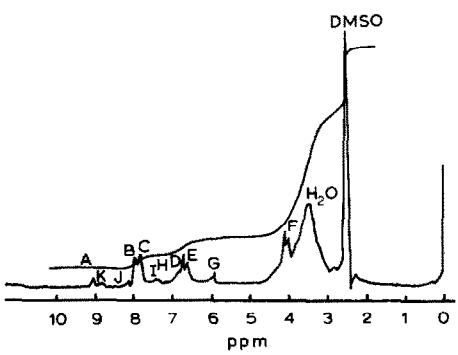

Fig. 4. ^{1}H spectrum of solid intermediate products at 212°C for the thermal decomposition of TBHTDD.

In the second stage, THTDD was decomposed at 212–224°C. The disappearance of the 1580 cm^{-1} and $\nu_{C=O}$(1800 cm^{-1}) bands showed that this step of the thermal decomposition process involved loss of two nitro groups attached to the nitrogen atoms adjacent to carbonyl. The theoretical weight loss corresponding to the formation of 2,8-dinitro-2,4,6,8,10,12-hexaazatricyclo(7,3,0,$0^{3,7}$)dodecane-5,11-dione (DHTDD) from THTDD is 12.8%. The experimental weight loss was 12.4%.

In the third stage, the IR spectra (Fig. 2) of the intermediate product at 246°C showed the disappearance of the 1575 cm^{-1} and 1270 cm^{-1} bands. The experimental value for the weight loss of 13.2% found between 224° and 246°C in the TG curve is in agreement with the theoretical weight loss of 13.3%, corresponding to the formation of 2,4,6,8,10,12-hexaazatricyclo(7,3,0,$0^{3,7}$)dodecane-5,11-dione (HTDD). These facts indicated that the intermediate product at 246°C had lost the two nitro groups at positions 2 and 8 in the molecule of DHTDD. The formation of these products from the original sample should be accomplished with a theoretical overall weight loss of 72.4%. In fact, this value of total weight loss for formation of these products was in agreement with the experimental value (Table 1) of 72.7%.

In the fourth stage, at the final decomposition temperature (410°C), an additional weight loss of 18.8% is observed in the TG curves (Fig. 1). This is due to the decomposition of HTDD to form a condensation product.

On the bases of experimental and calculated results, the thermal decomposition mechanism of TBHTDD is postulated to be as follows

$$\text{TBHTDD} \xrightarrow[120\text{–}212\,^\circ\text{C}]{-2CH_2C(NO_2)_3} \text{THTDD} \xrightarrow[212\text{–}224\,^\circ\text{C}]{-2NO_2} \text{DHTDD} \xrightarrow[224\text{–}246\,^\circ\text{C}]{-2NO_2}$$

$$\text{HTDD} \xrightarrow[246\text{–}400\,^\circ\text{C}]{} \text{condensation product}$$

ACKNOWLEDGEMENT

The authors wish to thank Professor Chang Mingnan for his helpful comments and suggestions in writing this paper.