

STUDIES ON THERMAL DEGRADATION OF BENZYLIDENE MALONONITRILES

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Abstract

Thermal decomposition studies have been carried out using flash vacuum thermolysis (FVT) to find out the decomposition temperature for benzylidene malononitriles (BMNs) including 2-chlorobenzylidene malononitrile (CS), a widely used riot control agent. The FVT studies have been carried out in a specially designed all glass assembly at various temperatures ranging from 300 to 600°C. A number of rearranged products along with hydrogen cyanide were obtained as major decomposition products. The products were analysed and the structures were confirmed by GC/MS. The thermal behaviour of BMNs has also been investigated by TG under nitrogen atmosphere. These studies show that the pyrotechnic mixture for tear gas munitions should not have burst temperature above 300°C.

Keywords: benzylidene malononitriles (BMNs), flash vacuum thermolysis (FVT), GC/MS, tear gas, TG

Introduction

Benzylidene malononitriles (BMNs) are the chief products of the condensation of benzaldehydes with malononitrile [1]. Derivatives of benzylidene malononitriles have important applications in various areas of chemistry. BMNs have received attention as cytotoxic agents against tumours [2, 3] and some of the derivatives are also used as rodent repellent [4, 5]. Derivatives of BMNs such as those containing bis-[2-chloroethyl] amino, bis-[chloromethyl] amino, bis-[chloromethyl] pyrrolidine and phenylazopyrimidine have also been used as chemotherapeutic agents against cancer [6, 7]. Certain other compounds have been used as pesticides, fungicides and insecticides [8]. Our interest in this group of compounds was largely due to the use of 2-chlorobenzylidene malononitrile (CS) as riot control agent [9].

2-Chlorobenzylidene malononitrile (CS) is discharged from the grenades/shells by burning a mixture of pyrotechnic composition. If the burst temperature of these munitions is high (>600°C), the irritants may decompose to unknown products. Therefore the thermal decomposition studies under controlled conditions are neces-

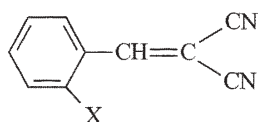
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sary in order to obtain optimum conditions. Such studies will throw light on the efficiency and stability of CS and other BMNs and will give an idea about the temperature of decomposition of BMNs. This is the first report on the thermolysis of BMNs.

Experimental

Materials

The BMNs having the general structure shown in Fig. 1 were synthesized by the condensation of equimolecular quantity of substituted benzaldehyde with malononitrile in cyclohexane in the presence of piperidine [10]. The compounds were purified by recrystallization and purity of each compound was found to range from 98–99% based on GLC analysis. The structures of BMNs were confirmed by IR, NMR and mass spectrometry. All chemicals were of analytical grade. The solutions were prepared in triple distilled water.



X = H **BMN**

X = Cl **o-chloro BMN**

X = F **o-fluoro BMN**

X = OCH₃ **o-methoxy BMN**

Fig. 1 General structures of BMN

Apparatus

A Shimadzu TCC-240 A spectrophotometer with silica cells of 1 cm path length was used for spectrophotometric measurements. A Shimadzu model GC-9 APTF gas chromatograph using capillary column BP-1 equipped with a flame ionisation detector and a chromatopak CR3A were used for the separation of decomposed products. A TSQ 7000 mass spectrometer coupled to Varian 3400 GC was used for GC/MS analysis of the pyrolysed mixture. A TGA-2950 CTA instrument was used for TG analysis.

Thermal decomposition

Thermal decomposition of BMNs was carried out in a specially designed all glass assembly (Fig. 2) and the decomposed products were collected in acetone. Various sets of experiments were carried out at fixed contact time (30 s) by varying the reactor temperature from 300 to 600°C. The percentage decomposition of BMNs was determined by GLC using capillary column BP-1 and decomposed products were separated and identified using GC/MS. The gaseous products i.e. hydrogen cyanide was

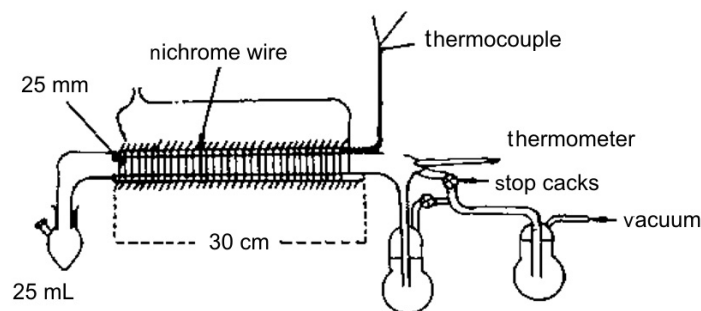


Fig. 2 All quartz assembly for flash vacuum thermolysis of BMNs

trapped in N/10 sodium hydroxide solution cooled with liquid nitrogen. Hydrogen cyanide was quantitatively estimated spectrophotometrically at $\lambda_{\max}=580$ nm after converting it into NaCN as per reported procedure [11].

GC/MS analysis

GC/MS analysis was performed in both EI and CI modes in order to identify the decomposition products. The GC conditions used were as follows; column BP-5 (30 m \times 0.32 mm) with a temperature programme of 80°C for 2 min followed by a gradient to 280 at 20°C min⁻¹. The injector temperature was maintained at 250°C while the transfer line was at 280°C. The EI analysis was performed at 70 eV with ion source temperature at 200°C and emission current of 400 μ A. The CI analysis was performed using methane as the reagent gas at a pressure of 4000 mT at 200 eV and emission current of 300 μ A.

TG analysis

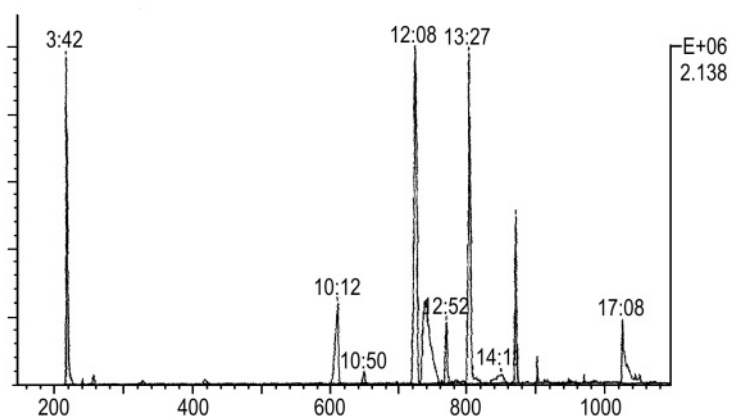
Thermal decomposition of BMNs was carried out under nitrogen atmosphere at a flow rate 40:60 and heating rate of 10°C min⁻¹. The sample size was 1.5 to 1.7 mg.

Results and discussion

The extent of decomposition of BMNs at different temperatures during flash vacuum thermolysis is depicted in Table 1. It was observed that substituted BMNs are stable upto 300°C and completely decompose at 600°C. Attempts were also made to identify the decomposition products by analysing them using GC/MS. The RIC of the pyrolysed BMN under chemical ionisation (CI) using methane as the reagent gas is shown in Fig. 3. It is evident from this figure that besides the unpyrolysed BMN at 12:08 min, many other products have been formed. The mass spectra of each of these peaks in both EI and CI modes were obtained in order to identify the compounds formed during thermolysis. Table 2 depicts different peaks in the RIC with corresponding pseudomolecular ions (M+H)⁺ obtained in CI, the EI mass spectral data and the compounds identified on the basis of their CI and EI mass spectra.

Table 1 Decomposition of BMN at different temperature

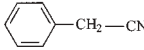
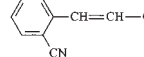
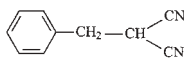
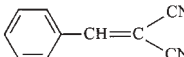
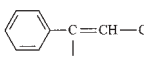
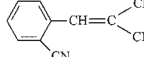
No.	X	Decomposition at different temperature/%			
		300°C	400°C	500°C	600°C
1	H	8.1	26.0	93.7	100
2	Cl	Nil	22.6	48.3	100
3	F	Nil	60.2	94.0	100
4	OCH ₃	Nil	96.0	98.0	100

**Fig. 3** RIC of pyrolysed BMN under GC/MS (CI)

It is evident from the identified compounds listed in Table 2 that BMN undergoes a variety of transformations under pyrolytic conditions. Besides unreacted BMN (**IV**, M^+ 154) eluting at 12:08 min; two other compounds having the same molecular mass (154) elute out at 10:12 and 13:27 min. The two compounds were identified as **II** and **V** respectively on the basis of their EI and CI spectral data. Benzyl cyanide (**I**) eluting at 03:42 was identified on the basis of its mass spectrum and its comparison with that obtained from authentic compound. The compound (**III**) eluting at 10:50 min produced a CI spectrum showing the molecular mass of the compound to be 156, indicating thereby that this compound is formed by the saturation of the double bond of BMN during pyrolysis. The compound eluting at 14:33 min is formed due to attachment of a cyanide radical at the α -position in the aromatic ring to give compound (**VI**). The EI spectrum of the compound corresponds well with the assigned structure. The compounds eluting at 15:04 and 17:08 could not be identified as the spectra obtained were not interpretable and showed unaccounted losses.

HCN was one of the major gaseous products formed during the decomposition of BMNs. It is in accordance with the literature reports that organic compounds containing nitrogen in the form of nitriles on decomposition give HCN [12, 13]. The

Table 2 Identification of the decomposition products from BMN by GC/MS (CI)

<i>Rt</i> /min	(M+H) ⁺ / <i>m/z</i>	Identification compounds
03:42	118	 I
10:12	155	 II
10:50	157	 III
12:08	155	 IV
13:27	155	 V
14:33	180	 VI
15:04	213	not identified
17:08	257	not identified

Substituted BMNs gave corresponding substituted compounds

amount of hydrogen cyanide formed by the degradation of *o*-chloro BMN (CS) as estimated spectrophotometrically is shown in Table 3. It is found that the percentage of HCN evolved increase with the increase in temperature.

Table 3 Spectrophotometric estimation of HCN from the decomposition of *o*-chloro BMN (CS)

S. No.	Decomposition temperature/°C	HCN/%
1	350	1.4
2	400	2.3
3	450	3.5
4	600	4.0

For other BMNs, only qualitative estimation was done by the same method

For the purpose of incineration, it is therefore, recommended that the temperature should be lower than 300°C. 2-Chloro BMN or CS is comparatively more stable than the fluoro and methoxy substituted BMNs. Furthermore, it is emphasised that full safety measures should be taken during the incineration of BMNs at high temperatures as hydrogen cyanide is one of the major toxic products formed.

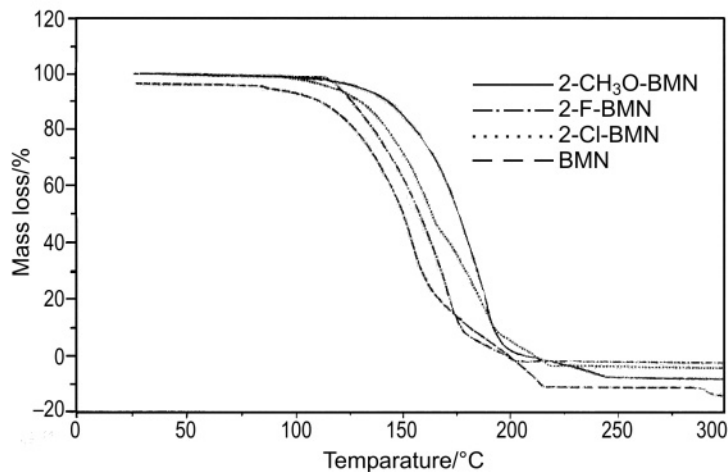


Fig. 4 TG curves of BMNs

Thermal decomposition studies of these BMNs were also carried out by TG under nitrogen atmosphere. The TG curves are shown in Fig. 4. It is clear from this figure that all these BMNs decomposes completely in the range of 125–225°C. These results however, do not agree with the one obtained from flash vacuum thermolysis which indicated complete decomposition only at 600°C. It is likely that some recombination of radicals takes place during FVT delaying the onset of degradation. Thus the thermogravimetric analysis of BMNs are not giving the true picture of decomposition. It is likely that these molecules sublimed prior to decomposition and hence remove the thermobalance parameters thereby showing mass loss. The order of stability of BMNs in the decreasing order is



Conclusions

Pyrotechnic mixture utilizing BMNs should be burnt below 300°C. HCN is one of the major products evolved during the decomposition and proper safety measures are therefore, recommended. The decomposition products formed on FVT have been identified by performing GC/MS analysis in both EI and CI modes. It has also been found that the degradation pattern of BMNs varies considerably in flash vacuum thermolysis as compared to thermogravimetric analysis in inert atmosphere.

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