Journal of Hazardous Materials 159 (2008) 630–635

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Short communication

Studies on thermal decomposition mechanism of CL-20 by pyrolysis gas chromatography–mass spectrometry (Py-GC/MS)

N.H. Naik[a], G.M. Gore[a], B.R. Gandhe[b], A.K. Sikder[a,*]

[a] High Energy Materials Research Laboratory, Sutarwadi, Pune 411021, India
[b] Directorate of Armament, DRDO Bhavan, New Delhi 110011, India

ARTICLE INFO

Article history:
Received 2 November 2007
Received in revised form 6 February 2008
Accepted 18 February 2008
Available online 23 February 2008

Keywords:
Pyrolysis GC/MS
CL-20
Tetraacetylhexaazaisowurtzitane
1,4-Dinitro piperazine
Decomposition mechanism

ABSTRACT

The thermal decomposition study of CL-20 (hexanitrohexaazaisowurtzitane) using pyrolysis GC/MS was carried out mainly by electron impact (EI) mode. Chemical ionization (CI) mode was used for further confirmation of identified species. Mass spectrum of CL-20 decomposition products predominantly revealed fragments with *m/z* 81 and 96 corresponding to $C_4H_5N_2^+$ and $C_4H_4N_2O^+$ ions, respectively. The total ion chromatogram (TIC) of CL-20 pyrolysis shows peak within first 2 min due to the presence of low molecular weight gases. Peaks corresponding to several other products were also observed including the atmospheric gases. Cyanogen formation (C_2N_2, *m/z* 52) observed to be enriched at the scan number 300–500. The low molecular mass range decomposition products formed by cleavage of C–N ring structure were found in majority. Additional structural information was sought by employing chemical ionization mode. The data generated during this study was instrumented in determining decomposition pathways of CL-20.

1. Introduction

Understanding of the complex physicochemical processes involved in the combustion and decomposition of energetic material is essential for the development of reliable model for performance, stability and hazard analysis of explosives. Identification of decomposition by-products is of prime importance in identifying toxic, hazardous and environment polluting species. The chemical decomposition mechanism, kinetic parameters and thermodynamic properties are the key factors in understanding ignition and combustion process and product distribution in explosion. Structural analysis of the fragments and intermediates resulting from controlled heating of energetic compounds can yield important information for understanding thermal decomposition processes. Moreover, the characterization of the individual products resulting from the combustion processes provides important data pertinent to the use of incineration process for disposal of absolute explosives and ammunition.

The newly developed caged nitramine 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,$0^{3,11}$,$0^{5,9}$]dodecane (CL-20) is a potential high energy compound likely to be used in advanced propellant and explosive formulations. Studies on thermal decomposition of CL-20 [1] have been reported by researchers, but studies based on pyrolysis gas chromatography coupled with mass spectra have not been reported.

Thermal decomposition of cage compound releases large amount of energy by way of bulk decomposition process and involves both unimolecular and bimolecular reactions. The complex chemical processes involved in the decomposition of cage structure of CL-20, make investigation more complex. An estimation of the influence of various parameters on the decomposition of the CL-20 is essential for design of efficient environmentally benign application of CL-20 in various formulations.

Pyrolysis in combination with various analytical techniques has been well reported in thermal decomposition studies of explosives [2]. Pyrolysis thin layer chromatography (Py-TLC) [3], pyrolysis atmospheric pressure ionization tandem mass spectroscopy (Py-API-MS-MS) [4–6], pyrolysis gas chromatography Fourier transform infrared spectroscopy (Py-GC-FTIR) and simultaneous thermogravimetry-modulated beam mass spectrometry [7–11] are well known techniques for study of thermal decomposition of explosives. Xiao and Yang [12,13] have studied the CL-20 ion dissociation mechanisms using mass analyzed ion kinetic energy spectrum (MIKE) and collision induced dissociation (CID). The pyrolysis gas chromatography–mass spectrometry (Py-GC/MS) technique employed in the present study provides unique advantage for identification of the pyrolyzates formed during decomposition of CL-20 at various temperatures. The technique incorporates the gas chromatograph for the separation of various

* Corresponding author. Tel.: +91 20 25869394; fax: +91 20 25869316.
E-mail address: ak_sikder@yahoo.com (A.K. Sikder).

0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2008.02.049

pyrolyzed products and mass spectrometer as an identification tool, to determine the thermal decomposition products and contributes to the understanding of the cage compound decomposition process and pathway. The pyrolysis GC/MS studies on CL-20 and its precursor like tetraacetylhexaazaisowurtzitane (TAIW) was carried out to obtain information on ring-opening reaction leading to the decomposition of cage structure.

In the present study, the thermal decomposition of CL-20 at 800 °C was investigated using pyrolysis GC/MS technique. Pyrolysis of 1,4-dinitro piperazine (1,4-DNP) was also carried out under identical conditions to look in to the decomposition pattern of six-membered ring.

2. Experimental

The CL-20, TAIW and 1,4-DNP were synthesized in laboratory as reported by Nielsen et al. [14] and Millar and Philbin [15]. Purity determined by HPLC and samples of 99% were used for further experimental purpose and ε-polymorph of CL-20 confirmed with IR [16]. Pyrolysis of the sample was carried out on CDS model 1000 pyroprobe (coil probe, sample taken in quartz capillary tube) under helium atmosphere. Pyrolyzer was connected to a gas chromatography (PerkinElmer, Clarus500) with split/splitless injector (75/1). Helium was used as carrier gas at a flow rate of 1 ml/min with back up pressure of 10 psi. An Elite-5 capillary column (30 m × 0.25 mm × 0.25 μm) was employed for the study with cross-bonded diphenyl-5% and dimethyl polysiloxane-95% as a stationary phase. Quadrupole mass spectrometer (PerkinElmer, Clarus500) hyphenated with GC was used to record the mass spectra of the corresponding chromatogram. Before its use, mass spectrometer detector (MSD) was calibrated using Heptacosane calibration standard while GC was calibrated with test mix-1 and test mix-2, as supplied by PerkinElmer.

About 0.3 mg of sample was placed in a quartz capillary tube of pyroprobe and the whole assembly was kept in the pyrolyzer for thermal decomposition at 800 °C for 15 s. Decomposed gaseous products from pyrolyzer were injected in GC with injector temperature at 225 °C. The GC oven temperature was programmed. Initially the oven was at 35 °C for 2 min. Then ramped at the rate of 10 °C/min to 250 °C and was maintained further for 17 min. The separated pyrolyzates from the GC were transferred to mass spectrometer (MS) via a heated interface which was at 200 °C temperature.

The mass spectrometer (MS) equipped with two different ion source modes, electron impact (EI) with energy 70 eV and chemical impact (CI) with energy of 30 eV was used. The ion source temperature for both EI and CI modes was maintained at 200 °C and methane gas was used for chemical ionization studies. MS was capable to scan 1–1200 amu within 100 ms. National institute of standard and technology (NIST) library was referred for identifying the pyrolyzed products. The fragments with match factor more than 90% were considered for comparison purpose.

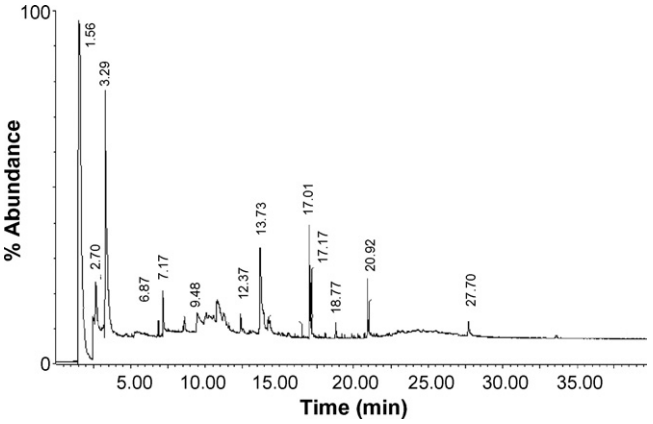

Fig. 1. Total ion chromatogram of CL-20's pyrolysis product on EI mode.

3. Results and discussion

The pyrolyzed products of CL-20 and its precursors were separated with the help of gas chromatography and analyzed by mass spectrometry using both EI and CI modes.

The GC/MS reconstructed ion chromatogram (RIC) of CL-20 revealed 13 distinguished peaks using EI mode (Fig. 1). The total ion mass spectrum (TIMS) of CL-20 using EI mode has been presented in Fig. 2 where base peak appeared at *m*/*z* 81 indicating the presence of $C_4H_5N_2^+$ ion. The full list of the molecular ions obtained in Py-GC/MS of CL-20 is given in Table 1. These results obtained are in concurrences with those reported by Pesce-Rodriguez et al. [17]. The first peak corresponds to unseparable low molecular weight gaseous species appeared within first 2 min. These peaks with their principal fragments and corresponding mass spectra are summarized in Table 1. Apart from these products 10 different products were observed, some of which could not be identified due to non-availability of reference spectra from NIST library. The total ion mass spectrum (TIMS) showed distinguished peaks at *m*/*z* 81, 96, 106 and 125 on Py-GC/MS in EI mode (Fig. 2). All these peaks substantiated the presence of substituted pyrazine products with a formula $C_xH_yN_z^+$ [18]. Presence of NO has been confirmed with *m*/*z* 30. The peak at *m*/*z* 28 and 44 indicate presence of N_2 and N_2O, respectively. The species with *m*/*z* 179, 213, 228 were observed as high molecular weight fragments in present pyrolysis experiment. As a consequence of decomposition of HCN, cyanogen (C_2N_2) formation at *m*/*z* 52 has been observed.

Table 1
Major peaks of CL-20 on EI mode with retention time and probable formulas

S. no.	RT	Scan	Major fragments (*m*/*z*)	Probable formula
1	1.56	300	27, 28, 30, 42, 43, 44	HCN, N_2, CO_2, N_2O, NO, C_2N_2
2	2.70	460	28, 32, 43, 44, 45, 61	–
3	3.29	560	27, 28, 52, 53, 54, 81	$C_4H_5N_2^+$
4	6.87	1169	28, 32, 44, 78, 104	$C_5H_3N_3^+$
5	7.17	1220	28, 32, 52, 53, 54, 79, 106	$C_6H_6N_2^+$
6	9.48	1612	28, 42, 43, 69, 96	$C_6H_4N_2O^+$
7	12.37	2102	28, 50, 75, 101, 128	$C_3H_6N_4O_2^+$
8	13.73	2334	28, 32, 40, 43, 68, 95, 121, 137	–
9	17.01	2891	39, 65, 75, 119, 151	–
10	17.17	2918	28, 32, 43, 77, 91, 133, 151, 179	–
11	18.77	3191	28, 32, 44, 73, 129, 185, 228	–
12	20.92	3555	28, 32, 44, 73, 97, 129, 157, 171, 185, 213	–
13	27.70	4707	28, 32, 44, 55, 57, 70, 149, 167	–