



Short communication

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

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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.

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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 decom-

position 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 spectrometry (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

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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 \times 0.25 mm \times 0.25 μ m) 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 identify-

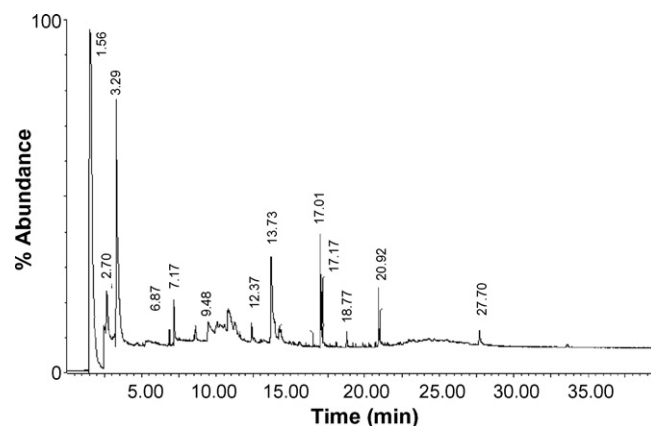


Fig. 1. Total ion chromatogram of CL-20's pyrolysis product on EI mode.

ing the pyrolyzed products. The fragments with match factor more than 90% were considered for comparison purpose.

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	–

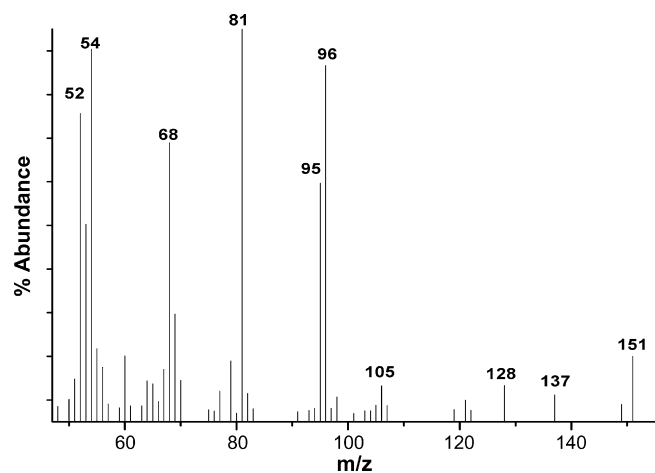


Fig. 2. Total ion mass spectrum (TIMS) of CL-20's pyrolysis product on EI mode.

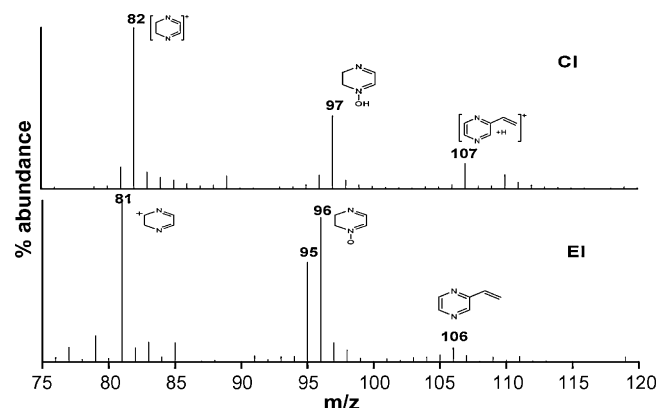


Fig. 4. Total ion mass spectrum of CL-20's pyrolysis product on EI (down) and CI (up) mode along with decomposition products.

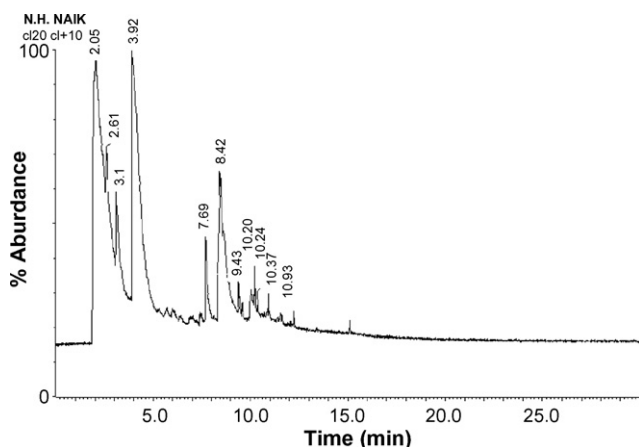


Fig. 3. Total ion chromatogram of CL-20's pyrolysis product on CI mode.

Py-GC/MS studies on CL-20 were performed using CI mode to get additional structural information and molecular ion peak of the pyrolysis products. Fig. 3 shows the total ion chromatogram of CL-20 using CI mode. The details of m/z values are presented in Table 2. Decomposition products of CL-20 using EI and CI modes are presented in Fig. 4. A base peak at m/z 81 in EI mode was due to the formation of $C_4H_5N_2^+$ which was further

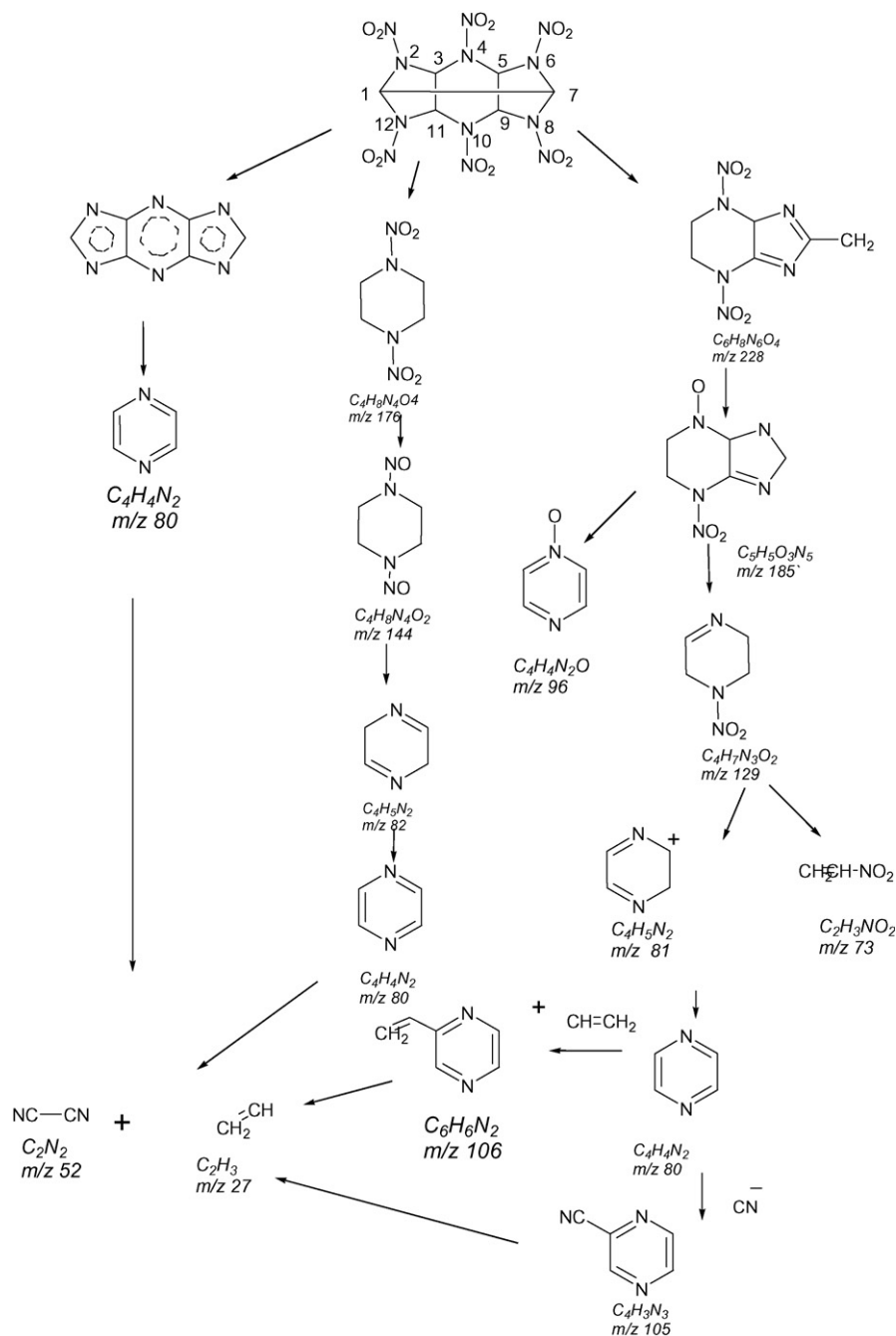
confirmed in CI mode as $M+1$. The other prominent peaks of CL-20 observed in EI mode at m/z 96, 104 and 106 were confirmed by NIST library. All these peaks confirm the presence of substituted pyrazine moiety, in the decomposition products of CL-20.

Okovytyy et al. [19] have predicted the decomposition pathway of CL-20 with the help of DFT (density functional theory) by using B3LYP (Becke's three parameters, Lee, Yang and Parr exchange) functional correlation. The hypothesis that [20] a molecular structure, under homologous conditions, determined preferred degradation pathways that can be theoretically predicted was examined in case of cyclic nitramines through semiempirical methods. The predicted decomposition products found to be substituted pyrazines, which supports our observation. It has also been reported [19] that the homolytic NO_2 group elimination from five-membered ring is least endothermic and CL-20 unimolecular decomposition results in the formation of the aromatic compound 1,5-dihydroimidazo[4,5-*b*:4'-5'-*e*]pyrazine. Three types of reaction pathways are well-reported for cyclic nitramines such as RDX and HMX during decomposition: (i) homolytic cleavage of an N–N bond accompanied by the elimination of the $-NO_2$ group, (ii) HONO elimination, and (iii) ring-opening reactions. Similar types of decomposition steps can be assumed for CL-20, as it belonged to the same class of cyclic nitramine compounds. The decomposition of both, five-membered rings and six-membered ring involves N–N bonds rupture processes, accompanied by the elimination of NO, NO_2 or HONO species which have been computed in the earlier studies.

The thermal decomposition pathway of CL-20 molecule is depicted in Scheme 1. The strained C_1 – C_7 bond joining the two 5-membered rings and 6-membered ring is primarily responsible for the stability of the skeleton. The decomposition of the cage appeared to commence with the loss of nitro groups via cleavage of N–N bond followed by breaking of C–N and C–C bonds. Since the molecular structure of CL-20 consists of two types of NO_2 groups, the preferential elimination of one type of NO_2 group over the other is quite possible. Further C–N bond breaking led to the formation of molecular mass species in the range of m/z 80–110 and these were assigned to substituted pyrazine derivatives. Some of these fragments further decomposed to lower molecular mass fragments such as H_2O , HCN, CO, HNC, CO_2 and C_2N_2 . The thermogravimetry mass spectrometer (TG-MS) study [20] of CL-20 reports evolution of gases like, HCN, CO, CO_2 , HNC and N_2O which supports our observation. In the present study, it was observed that no stable substituted five-membered ring species

Table 2
Major peaks of CL-20 on CI mode with retention time and probable formulas

S. no.	RT	Scan	Major fragments (m/z)	Probable formula
1	2.05	234	45, 53	CO_2 , C_2N_2
2	2.607	298	45, 71	–
3	3.106	355	45, 61, 89	–
4	3.920	448	82	$C_4H_5N_2 + H$
5	7.691	879	107	$C_6H_6N_2 + H$
6	8.426	963	97, 125	$C_6H_4N_2O + C_2H_5$
7	9.432	1078	126	–
8	10.20	1166	45, 57, 71, 83, 85, 97, 111	$C_6H_4N_2O + CH_3$
9	10.24	1171	140	–
10	10.37	1186	83	$C_4H_5N_2 + 2H$
11	10.93	1250	125, 111, 97, 85, 83, 71, 57, 45	$C_6H_4N_2O + C_2H_5$, $C_6H_4N_2O + CH_3$



Scheme 1. Decomposition mechanism of CL-20.

was formed during decomposition of CL-20 under given Py-GC/MS conditions.

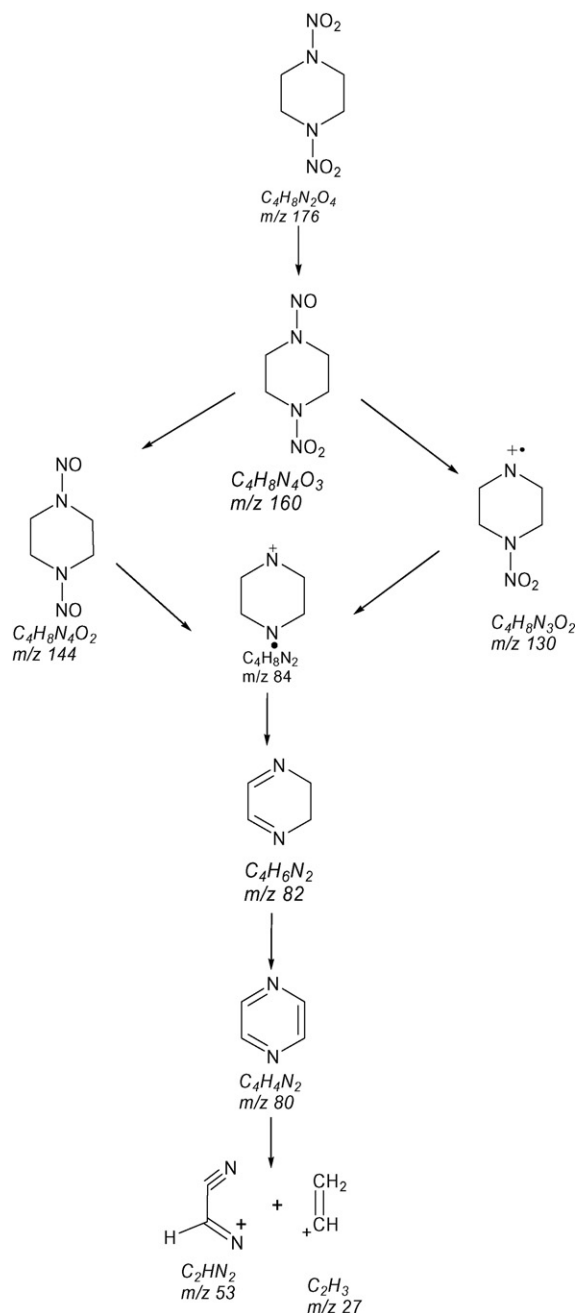
In the main fragmentation pathway (Scheme 1), the C–N bond breakage of five-membered rings also appeared to occurred keeping six-membered ring intact. This is envisaged in case of a fragmented ion at m/z 96 ($C_4H_4N_2O^+$), which further decomposed to pyrazine (m/z 80) with the elimination of oxygen atom. The cleavage of bond between carbon and nitrogen atoms of five-membered rings was mainly responsible for yielding of most of the fragments. Substituted pyrazine fragments observed in the pyrolysis study also suggested the presence of six-membered ring.

To further confirm this decomposition mechanism, the pyrolysis GC/MS study was also carried out for 1,4-DNP; a structurally similar

Table 3

Major peaks of 1,4-dinitro piperazine (1,4-DNP) on EI mode with retention time and probable formulas

S. no.	RT	Scan	Major fragments (m/z)	Probable formula
1	1.59	272	27, 28, 30, 44, 52	N_2 , NO, CO_2 , C_2N_2
2	4.243	722	26, 53, 80	$C_4H_4N_2^+$
3	6.014	1023	28, 32, 67, 94	$C_5H_6N_2^+$
4	8.608	1464	26, 28, 32, 51, 78, 105	$C_5H_3N_3^+$
5	8.803	1497	28, 32, 68, 82	$C_4H_6N_2^+$
6	10.01	1702	28, 32, 41, 68, 95	$C_4H_5N_3^+$
7	10.69	1818	28, 32, 41, 53, 80, 96	$C_4H_4N_2O^+$
8	15.05	2559	28, 42, 55, 84, 114, 144	$C_4H_8N_4O_2^+$
9	15.81	2688	42, 82, 149	–
10	16.32	2775	28, 42, 55, 56, 84, 130, 144, 160	$C_4H_8N_4O_3^+$
11	17.49	2972	28, 32, 42, 55, 56, 57, 84, 130, 160, 176	$C_4H_8N_4O_4^+$

**Table 4**

Major peaks of tetraacetylhexaazaisowurtzitane (TAIW) on EI mode with retention time and probable formulas

S. no.	RT	Scan	Major fragments (<i>m/z</i>)	Probable formula
1	1.21	207	28, 32, 44	N ₂ , CO ₂ , N ₂ O,
2	1.59	272	27, 28, 44, 64	HCN, N ₂ , CO ₂ ,
3	1.86	318	40, 41, 58, 69	C ₃ H ₄ N ₂
4	3.07	523	43, 45, 60	CH ₃ COOH
5	4.05	690	43	(CH ₃ CO) ₂ O, C ₂ H ₅ NO
6	4.17	709	26, 53, 80	C ₄ H ₄ N ₂
7	5.90	1003	28, 42, 43, 44, 59	CH ₃ CONH ₂ , (CH ₃ CO) ₂ NH
8	6.06	1030	28, 41, 67, 94	2-Ethenyl 1 <i>H</i> -imidazole, methyl pyrazine
9	8.64	1469	26, 51, 78, 105	C ₅ H ₃ N ₃
10	9.54	1622	43, 53, 80, 93, 107, 122	C ₆ H ₇ N ₂ O ⁺
11	10.01	1702	43, 68, 82, 104, 110	C ₅ H ₆ N ₂ O

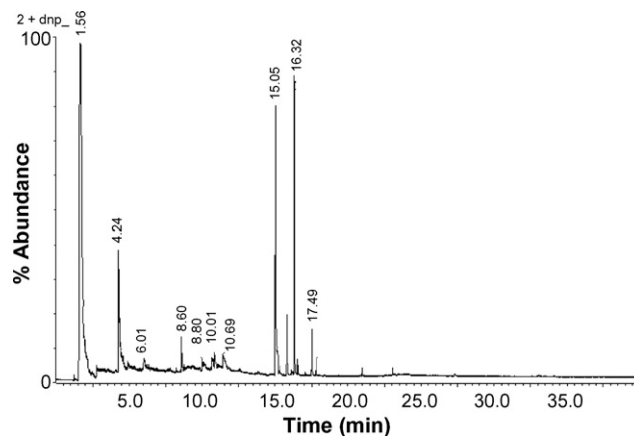


Fig. 5. Total ion chromatogram of 1,4-dinitro piperazine pyrolysis product on EI mode.

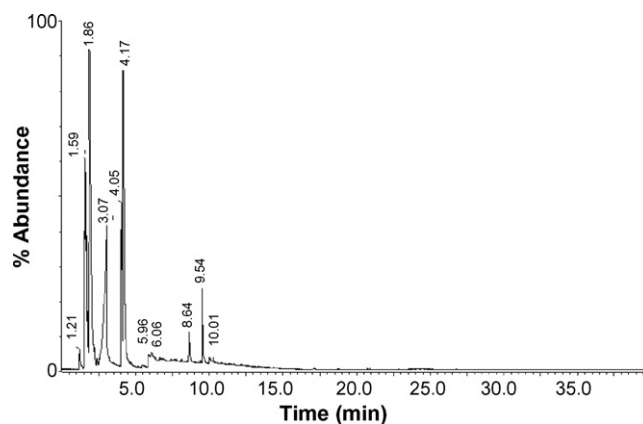


Fig. 6. Total ion chromatogram of tetraacetylhexaazaisowurtzitane pyrolysis product on EI mode.

cyclic six-membered nitramine compound (Fig. 5). The base peak obtained at *m/z* 80 was due to the formation of pyrazine (C₄H₄N₂) (Table 3). Fragmentation of which, resulted into species having low molecular weights up to *m/z* 53, 44 and 27. It is similar to molecular ions obtained in Py-GC/MS of CL-20 in EI mode. This substantiated the formation of stable six-membered ring during decomposition of CL-20 and DNP both (Scheme 2).

Further, in order to determine the decomposition process of cage structure, in absence of nitro groups, thermal decomposition of one of the CL-20 precursor, tetraacetylhexaazaisowurtzitane (TAIW) has been studied under similar conditions. The total ion chromatogram of TAIW showing 11 peaks (Fig. 6) and the corresponding *m/z* values along with its fragmentation pattern are presented in Table 4. The base peaks appeared at *m/z* 60 and 43, were due to the formation of acetic acid and acetic anhydride from decomposition of the four acetyl groups present in TAIW. Another predominant peak with *m/z* 80 was observed representing the pyrazine species.

Thus, CL-20 and TAIW have the same cage structure and pyrazine and *N*-oxo-pyrazine as the major fragments, realized during their pyrolysis. This confirms that both the compounds follow same fragmentation pathways.

4. Conclusion

Pyrolysis of CL-20 at 800 °C was studied. GC/MS was used for identification of the decomposition products. It appears that

the cleavage of C–N bond of the cage structure of CL-20 resulted in formation of low molecular weight decomposition products. Mass spectrometry results revealed that prominent decomposition fragments with m/z 81 and 96 were $C_4H_5N_2^+$ and $C_4H_4N_2O^+$, respectively. Cyanogen (C_2N_2) with m/z 52 was also appeared along with low molecular weight gaseous products. The probable decomposition pathway is proposed for CL-20, to provide better insight to the combustion phenomenon in case of CL-20 as well as CL-20-based compositions.

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