

Establishment of process technology for the manufacture of dinitrogen pentoxide and its utility for the synthesis of most powerful explosive of today—CL-20

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Abstract

This paper reviews the recent work done on the synthesis as well as characterization of dinitrogen pentoxide (DNPO). The physico-chemical characteristics of DNPO are also discussed. The review brings out the key aspects of N_2O_5 technology with relevance to realize modern and novel HEMs. The paper also includes the aspects related with establishing the synthesis facility of dinitrogen pentoxide at HEMRL by gas phase interaction of N_2O_4 with O_3 . The process parameters for the synthesis of N_2O_5 at 50 g/batch have been optimized. The synthesized dinitrogen pentoxide has been characterized by UV [204, 213, 258 nm ($\pi \rightarrow \pi^*$) 378 and 384 nm ($n \rightarrow \pi^*$)] and IR (1428, 1266, 1249, 1206, 1044, 822, 750, 546 and 454 cm^{-1}) spectroscopy. The DSC clearly showed the sublimation of N_2O_5 at 32°C . The nitration studies on 2,6,8,12-tetraacetylhexaaza tetracyclo[5,5,0,0^{3,11}0^{5,9}]dodecane (TAIW) proved its viability in 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) synthesis. The synthesized CL-20 and its precursors have also been subjected to hyphenated TG-FTIR studies to understand decomposition pattern.

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1. Introduction

The nitrated products find broad spectrum of applications in the area of high energy materials (HEMs) [1,2], pharmaceuticals and fertilizers. A series of nitrated products, namely octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 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) 1,3,3-trinitro azetidine (TNAZ), octanitrocubane (ONC), ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF), are key HEMs. The selection of a nitrating agent for a particular nitration reaction is mainly dependent on the chemical nature of substrate molecule. The most commonly used nitrating agent is a relatively inexpensive mixture of concentrated nitric acid and sulphuric acid in different proportions.

However, conventionally used nitrating agents pose serious pollution threat to the environment and meet with failure in case of deactivated substrates or selective nitration needs. Nitronium tetrafluoroborate and nitronium hexafluorophosphate are found effective nitrating agents for deactivated substrate molecules. Suzuki et al. [3,4] reported selective nitration of certain aromatics using $N_2O_4/O_3/O_2$ mixtures. $(CF_3CO)_2O/HNO_3$ can also be used for selective nitration of certain deactivated substrates. However, it is not recommended because of explosion hazards involved during its use for nitration reactions.

This calls for the search of versatile cost effective nitrating agents for the synthesis of HEMs. Although, N_2O_5 has been known for almost 150 years (1849) [5], its very limited application has been made as a nitrating agent. None of the publications in open literature disclose the finer details of actual process for the synthesis of dinitrogen pentoxide in a crystal clear form due to its strategic importance.

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Advantages of using dinitrogen pentoxide in comparison to conventional nitrating agents are: (a) high selectivity in position of attack with poly functional substrates, particularly when used in organic solvents; (b) feasibility towards the reaction in acidic medium to offer strong nitrating system; (c) simple isolation of the product; (d) ease of temperature control; (e) very high yields (80–90%); (f) absence of spent acid for disposal.

The non-selective nitration by N_2O_5 in acidic medium can be exploited to nitrate deactivated precursors [6–8] while nitration by N_2O_5 dissolved in an organic solvent (especially chlorinated hydrocarbons) is an effective means for selective nitration of substrates where there is more than one possible nitration site in the molecule. This unique dichotomy of dinitrogen pentoxide chemistry may lead to a wide variety of products of interest to energetic materials community and has accelerated R&D efforts towards utilizing the potential of dinitrogen pentoxide as nitrating agent. The recent work carried out on synthesis, characterization and its utility as nitrating agent is summarized in the following text.

1.1. Synthesis/production of N_2O_5

Dinitrogen pentoxide can be generated by adopting different approaches. Solid N_2O_5 can be prepared on a laboratory scale by the reaction of chlorine with solid silver nitrate as well as during the reaction of nitryl chloride/fluoride with metal nitrate and by the dehydration of nitric acid by phosphoric oxide [9,10]. However, these methods produce low yields of poor quality product contaminated with N_2O_4 and small quantities of HNO_3 . Electrochemical synthesis of dinitrogen pentoxide by controlled potential oxidation (approximately +1.85 V) of dinitrogen tetraoxide in anhydrous nitric acid at platinum or titanium supported iron oxide anodes is established by several researchers [11–13].

The N_2O_5 is generated along with HNO_3 in electrochemical process. It can be isolated by cooling the solution. U.K. Patent [14] reports that mixture of $N_2O_4 + N_2O_5$ can be easily separated by adding organic solvent (CH_2Cl_2) followed by chilling, to crystallize N_2O_4 and obtain dinitrogen pentoxide solution in dichloromethane after its separation. Various other approaches [15,16] are proposed to isolate N_2O_5 from its mixture with N_2O_4/HNO_3 . A dielectric packed pellet-bed plasma reactor can also be used as an efficient method for the synthesis of N_2O_5 . The reactor is packed with glass beads and operates at high frequency (10–13 Hz) and high voltage (<30 kV). Typically, the reaction energy level is 38 J L^{-1} and converts 45 ppm of NO_2 into 53 ppm of N_2O_5 at the energy cost of $\sim 180 \text{ eV}$ for every molecule of N_2O_5 produced. Recently, a new simple method of quantitative synthesis of N_2O_5 has been reported by Wilson and Christie [17]. It involves the reaction of FNO_2 with an excess of $LiNO_3$ at 0°C .

Preparation of N_2O_5 by reacting N_2O_4 with ozone is considered one of the most versatile methods to obtain high purity N_2O_5 [18,19] in inert organic solvent at -20 to -30°C . A

Table 1

Physical and thermo-chemical characteristics of ozone, and N_2O_4 and N_2O_5

Property/parameter	N_2O_4	O_3	N_2O_5
Molecular weight	92.011	48.0	108.02
Specific gravity, gas at 20°C (air = 1) (g/cm^3)	3.17	1.655	3.725
Liquid density (g/cm^3 at 20°C)	1.448	–	Sublimes
Melting point ($^\circ\text{C}$)	-9.3	-192.5	30
Normal boiling point ($^\circ\text{C}$)	21.3	-111.9	32.4
Standard free energy of formation ($\text{kcal} (\text{g mol})^{-1}$)	23.41	38.88	–
Standard heat of formation ($\text{kcal} (\text{g mol})^{-1}$)	2.23	33.88	-10.0

plant manufacturing N_2O_5 at 360 g/h by the gas phase oxidation of N_2O_4 with ozone is operative at Indian Head Division [20] of Naval Surface Warfare Center (NSWC), USA.

1.2. Characterization

The physico-chemical properties of N_2O_5 , N_2O_4 and O_3 are given in the Table 1. N_2O_5 is a thermally labile white crystalline solid. It has half life of 10 days at 0°C and that of 10 h at 20°C . UV absorption [21] of N_2O_5 results in maxima at λ_{max} 200 and 380 nm (at 223–300 K). Vacuum ultraviolet spectrum of N_2O_5 shows [22] absorption at λ_{max} 150–240 nm at $195 \pm 3 \text{ K}$. The lack of sharp features suggest that the excitation of N_2O_5 results in its dissociation over the selected wavelength range of spectrum studied. The microwave spectrum [23] of dinitrogen pentoxide does not exhibit reproducible transitions. Bencivenni et al. [24] reported IR frequencies of N_2O_5 in the region of 200–4000 cm^{-1} region. The gas phase FTIR spectrum [25] of N_2O_5 exhibited peaks in the region of 8.1–5.7 m. The total intensities of N_2O_5 bands located at 8.1 and 5.7 m were $I_{N_2O_5} = 1280$ and 3250 cm^{-1} , respectively. Hajorth et al. [26] measured absolute intensities of the N_2O_5 (710–780, 1225–1270 cm^{-1}). It has been established that integrated band strengths and absorbance cross-sections per molecule have no significant dependence on temperature [27].

The IR spectrum [28,29] of dinitrogen pentoxide on gold foil determined at 80 K suggests its amorphous co-valent nature as well as the crystal phase order with molecular planes perpendicular to the surface. Domenech et al. [29] also carried out infrared and microwave molecular beam studies on N_2O_5 to provide support to its C_2 symmetry. IR spectra using laser spectrometer revealed N–O stretching fundamental band at 1246 cm^{-1} . The laser Raman Spectrum of solid N_2O_5 suggests that NO_2 cation in solid N_2O_5 might not be completely linear [17]. The time of flight (TOF) mass spectral studies detected NO_2^+ , NO^+ , O^+ and N^+ as fragmentation products [30,31].

1.3. Photo/thermal decomposition

The gas phase photo decomposition [32–35] of N_2O_5 was studied by UV spectrophotometer at 254 nm. Ultraviolet

(UV) photolysis [36] of N_2O_5 matrix (at 4.2 K) at intensity (I) >230 nm is reported to result in the photo reduction of N_2O_5 to N_2O via N_2O_3 as an intermediate. In argon matrices, both asymmetric and symmetric N_2O_3 were formed whereas in solid nitrogen only asymmetric N_2O_3 was produced. Visible fluorescence from electronically excited NO_2 was observed on photolysis [37] of N_2O_5 in the wavelength region of 266–304 nm. NO_2 was detected in the excited electronic state during initial decomposition phase.

The variation in the yield of CO_2 as function of reactant composition and time as a result of the gas phase reaction of CO by N_2O_5 at 291–343 °C is also investigated [38]. It is observed that the known intermediates in the decomposition of N_2O_5 do not contribute to the formation of CO_2 and a peroxy radical species ($-ONOO$) is involved. Chichirov et al. [39] determined the decomposition rates of N_2O_5 in HNO_3 (over the entire homogeneous solution composition range) in the temperature region of 388 K and reported apparent activation energy of 131 kJ mol^{-1} . The increased thermal stability of N_2O_5 in HNO_3 is explained on the basis of its solvation.

The kinetics of unimolecular decomposition of dinitrogen pentoxide in presence of excess of nitric oxide in a bath of nitrogen was studied as a function of temperature and pressure with the aid of FTIR. The data [40] obtained brings out that the calculated atmospheric decomposition life times for N_2O_5 are decreased to the extent of ~15–20% in the upper stratosphere compared to ground level.

Willington and Japar [41] studied the kinetics of reaction of HNO_2 with N_2O_5 using FTIR spectroscopy and estimated the rate constants for observed decay of HNO_2 as $7.10^{-19} \text{ cm}^3 \text{ mol}^{-5}$. Equilibrium concentrations of NO_3^- and NO_2^+ ions have been determined [42] in 7.15–24.1 weight (wt.%) N_2O_5 solutions in HNO_3 and dissociation of

N_2O_5 was observed in solutions containing >15 wt.%. Combination of the experimental data with an improved value for the entropy of formation of NO_3 by Burrows et al. [43] reports a value of $17.5 \pm 1.0 \text{ kcal mol}^{-1}$ for dissociation of dinitrogen pentoxide at 298 K. Kurbatov and Skorokhodov [44] evaluated the published data and concluded that a heteroazeotropic equilibrium containing HNO_3 (1–2 wt.%) at 760 Torr and $\sim 30^\circ\text{C}$ exists in the title system. They also depicted the phase diagram.

1.4. DNPO: a versatile nitrating agent

Synthesis of a variety of inorganic [45–50] and organic compounds [51–98] using N_2O_5 is reported in literature. Wide ranging applications of N_2O_5 in synthesis of HEMs and allied materials are summarized in Tables 2–4.

In view of the increasing importance of N_2O_5 as nitrating system for realizing novel HEMs and allied materials, a program was undertaken to establish synthesis facility of N_2O_5 at HEMRL. Approach based on interaction of N_2O_4 and O_3 to obtain N_2O_5 in pure form was selected during this work.

However, the method poses challenges due to involvement of gas phase reaction. The criticality of the process is that both the reactants and the product in this process are of gaseous nature. Owing to difference in the densities of the reactants, there are major challenges such as difficulty in heat transfer, segregation/de-mixing of the reactants and the condensation of the product. The expertise of scientists from National Chemical Laboratory (NCL), Pune, India, in gas phase reactions was effectively utilized to provide design solution. The synthesized N_2O_5 was characterized and feasibility of N_2O_5 aided nitration was studied on tetraacetylisowurtzitane (TAIW)

Table 2
An outline of N_2O_5 aided HEMs synthesis by harsh nitration reported by various researchers

S. no.	Substrate	Reaction conditions	Product	Ref. no.
1	1,5-Diacetyl octahydro-3,7,-dinitro-1,3,5,7-tetraazocine	N_2O_5 in HNO_3 , 70 °C, 10–50 min	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) (82%)	[51]
2	Tetra acetyl tetraazacyclo octane	N_2O_5 in HNO_3 , 30–35 °C	HMX (79%)	[51]
3	Hexamethylene tetramine (HMT)	N_2O_5 in HNO_3 , –20 °C, 30–60 min	1,3,5-Trinitrozo-1,3,5-triaza cyclohexane (RDX) (32%) RDX (57%)	[52]
4	HMT	40 eq. 25% N_2O_5/HNO_3 in CCl_4 , –20 °C, 30 min (57%)	RDX	[53]
5	Dinitroglycouril (DINGU)	N_2O_5 in HNO_3 , 10 °C, 30–60 min	Tetranitroglycouril (TINGU)	[54]
6	Mono furazano piperazine/1,4-ditertiary butyl monofurazano piperazine	Trifluoroacetic anhydride (TFAA)/ N_2O_5/HNO_3 , 0 °C	Dinitro monofurazano piperazine (DNMFP)	[55]
7	2,4,6-Triaza cyclohexanone	N_2O_5 in 100% $HNO_3/TFAA$, –10 °C, 5 min (43%)	2,4,6-Trinitro-2,4,6-triazacyclohexanone (K-6)	[56]
8	7-Acetyl-2,5-dinitro-2,5,7,9-tetraazabicyclo (4.3.0)nonane-8-one	(i) 20% N_2O_5 in HNO_3	No reaction	[57]
		(ii) TFAA/20% N_2O_5 in HNO_3	No reaction	
		(iii) 20% N_2O_5 in HNO_3	No reaction	
		(iv) TFMSAA	2,5,7,9-Tetranitro-2,5,7,9-tetraazabicyclo(4.3.0)nonane-8-one (69%) (K-56)	

Table 3
HEMs obtained by N₂O₅ aided nitrations

S. no.	Substrate	Reaction conditions	Product	Ref. no.
9	Heptanitrocubane (HNC)	N ₂ O ₅ , LiN(TMS) ₂ or NaN(TMS) ₂ /NOCl/O ₃ , Dichloromethane (DCM), –78 °C	Octonitrocubane (ONC) (45–55%)	[2]
10	Triazene	N ₂ O ₅ in CH ₃ NO ₂ , 0 °C, 30 min	Ammonium dinitramide (ADN) (50%)	[58]
	Ammonia	N ₂ O ₅ in DCM/NH ₃ , –20 °C, 3 h		[59]
	Ammonium nitro urethane			[60]
11	Hydroxymethyl methyl oxetene (HMMO)	N ₂ O ₅ in DCM, –10 °C, 30–60 min	Nitratomethyl methyl oxetene (NIMMO)	[61–64]
12	3-Hydroxymethyl-3-methyl oxetane, 1,4-butane-bisepoxide and bis epoxide	N ₂ O ₅ , DCM 30–40 min	Trimethylolthane trinitrate, octane tetrol tetranitrate and erythritol tetranitrate	[63]
13	3-Phenyl oxetane	N ₂ O ₅ , DCM, –60 to 0 °C, 5–30 min (80%)	2-Arylpropane-1,3-diol dinitrate	[65]
14	Epoxides/oxetenes	N ₂ O ₅ , DCM, –5 °C to 20, 5–270 min (55–97%)	Nitrate esters	[64]
15	Aziridines and azetidines	N ₂ O ₅ , DCM, –5 to 5 °C, 1.5–3 hr.	Nitrate derivatives	[64,66–70]
16	Hydroxy terminated polybutadiene (HTPB)	N ₂ O ₅ in DCM	Nitrated HTPB (yield 90%)	[71]
17	Glycidol	N ₂ O ₅ in DCM, –10 °C, 30–60 min	Glycidyl nitrate (GLYN) (99%)	[72,73]

Table 4
Utilization of N₂O₅ based nitrations for allied materials

S. no.	Substrate	Reaction conditions	Product	Ref. no.
18	Hydroxy telechelic polyglycidol	N ₂ O ₅ , DCM 10–15 min	Hydroxy telechelic polyglycidyl nitrate	[74]
19	Epoxides	N ₂ O ₅ , DCM, 5–20 °C, 5–27 min (73–96%)	Vicinal nitrate ester	[75]
20	Epoxy alcohol	N ₂ O ₅ , DCM	Epoxy nitrates	
21	RR'NNR''SiMe ₃	N ₂ O ₅ , DCM 30–40 min	RR'NR''NO ₂ and their salts	[76]
22	Silylamines and silylethers	N ₂ O ₅ , DCM, –5 to 10 °C, 0.5–18 h (35–92%)	Nitramines and nitrate esters	[77]
23	2-Methyl-2-hexanol, <i>o</i> -silylethers and silylamines	N ₂ O ₅ , DCM 45 min	NIMMO, poly NIMMO (3-nitratomethyl-3-methyl oxetane), GLYN, cyclodextrin nitrate and HMX	[78]
24	Silylethers	N ₂ O ₅ , DCM 30 min	Nitramines/nitrate esters	[79]
25	Hydroxyalkyl substituted cyclic ether	N ₂ O ₅ , DCM 40 min	Nitroalkyl substituted cyclic ethers	[80]
26	<i>N</i> -(Trialkyl silyl) ethers	N ₂ O ₅ , DCM	Nitramines and nitramides	[81]
27	Cellulose	N ₂ O ₅	Cellulose nitrate	[82]
28	Pyrene/anthracene	N ₂ O ₅ , organic solvent	Nitro derivatives	[83]
29	Diaminofurazan	N ₂ O ₅ , DCM 60 min	Dinitrofurazan	[84]
30	Substituted pyridines	N ₂ O ₅ , organic solvent	Mixture of nitrated products	[85]
31	4- <i>R</i> -Substituted styrenes, R = H, Me, Cl, CF ₃ , NO ₂	N ₂ O ₅ , dry DCM, –45 °C (99%)	Mixture of nitrated product (1-aryl-2-nitro ethylnitrate, 1,2-dinitro-1-aryl ethane, 1,2-dinitrato-1-aryl ethane and 2-aryl-2-nitroethylnitrate).	[86]
32	R–C(=N–OH)–OMe (R = Ph, <i>p</i> -NO ₂ C ₆ H ₄ , <i>m</i> -O ₂ NC ₆ H ₄)	N ₂ O ₅ , DCM	Aryl dinitromethoxymethanes	[87]
33	Trinitrotriazine	N ₂ O ₅ , DCM	<i>cis</i> and <i>trans</i> Trinitrotriazines	[88]
34	Selective para nitration of aromatic compounds	N ₂ O ₅ , DCM	Nitro derivatives	[89]
35	Pyrimidine	(i) N ₂ O ₅ , dry CH ₃ NO ₂ , 0 °C, 5–30 min under N ₂ (80%); (ii) methyl alcohol	2,4-Dialkoxy-1,3-dinitro-1,2,3,4-tetrahydropyrimidine	[90]
36	1,2,4-Trichloro-5-nitrobenzene	N ₂ O ₅ /nitronium trifluoromethane sulphonate/HNO ₃ , 30 °C (58–96%)	1,2,4-Trichloro-3,5-dinitrobenzene	[91]
37	2,4,6-Triethylene melamine	N ₂ O ₅ in DCM, 0–5 °C, 1–2 h	2,4,6-(<i>N</i> -Nitro-ethyl nitrate)-triazine (Tris-X) (95%)	[92]
38	Fluoranthene	N ₂ O ₅ , CCl ₄ , 25 °C, 5 min (78%)	2-Nitrofluoranthene and 1,2-dinitrofluoranthene	[93]
39	<i>p</i> -Benzoquinone dioxime	N ₂ O ₅ , DCM 30–45 min	<i>p</i> -(NO ₂) ₂ C ₆ H ₄	[94]
40	Substituted benzaldehydes	N ₂ O ₅ , organic solvent	Nitration and oxidation products	[95]
41	Tetraazadecalin	N ₂ O ₅ , DCM	<i>trans</i> -1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin	[96]
42	1,2- or 1,3-Diol	N ₂ O ₅ , organic solvent 30 min	1,2 and 1,3 Dinitrate esters	[97,98]

towards synthesis of 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, HNIW) which is considered the most powerful explosive of today. In view of its superior performance, CL-20 is emerging as the next generation HEM. Its attributes of great interest are higher density ($\rho > 2 \text{ g/cm}^3$) and heat of formation ($\Delta H_f \sim 100 \text{ kcal mol}^{-1}$) than that of cyclo tetramethylene tetranitramine—HMX ($\rho 1.91 \text{ g/cm}^3$ and $\Delta H_f + 17 \text{ kcal mol}^{-1}$, respectively) due to strained cage structure carrying six $-\text{NO}_2$ substituents. Production technology breakthrough by Thiokol Corporation, USA and SNPE, France resulted in its emergence as a superior viable alternative [99] to HMX.

Nielsen et al. of NAWC, USA, first reported the synthesis of CL-20 in 1987 using nitrosonium/nitronium tetrafluoroborate as a nitrating agent [100–102]. The nitration of tetraacetyl isowurtzitane (TAIW) and tetraacetyl diformyl isowurtzitane (TADFIW) with a mixture of nitric and sulphuric acid has been reported [104–107] for the synthesis of CL-20.

HEMRL, India, also has been pursuing research programme on the synthesis of CL-20 in the recent past. Initial efforts were concentrated on the synthesis of CL-20 using nitronium/nitrosonium tetrafluoroborate as a nitrating agent [108]. Currently, in HEMRL, efforts are being focused on establishing cost effective synthesis process for CL-20. In this direction, globally efforts are on to reduce the cost of catalyst and nitrating agent. It is also well documented that N_2O_5 in combination with 100% HNO_3 acts as a more powerful nitrating agent than 100% HNO_3 or $\text{HNO}_3/\text{H}_2\text{SO}_4$ system [109]. In view of the above observations and continued research and development [110–113] interest on CL-20 in HEMRL, initial feasibility studies on the synthesis of CL-20 using N_2O_5 in combination with HNO_3 was undertaken in the present study.

2. Experimental

2.1. Lab scale synthesis set up: design aspects

Lab scale plant installed at HEMRL for generating N_2O_5 in solid form has working capacity of 200 g/h to match the ozone generator capacity of $\sim 160 \text{ g/h}$. The plant has modular design and comprises of (i) feed, (ii) reactor, (iii) product and (iv) control module.

The feed module consists of the ozone generator as well as N_2O_4 container connected to expansion tank and provided with an IR lamp for warming the container to ensure its smooth flow at low temperatures encountered during the variation of the order of $+5$ to $+40^\circ\text{C}$ in ambient temperature. The reactor module has four sub modules (reactors) in parallel to accommodate varying demand of N_2O_5 (20–200 g). The reactors are jacketed for counter-current flow of coolant (chilled water). The product module consists of four coolers and two chiller-cum-collectors. It is in line with cold finger

condenser and a gas scrubber for safe disposal of oxygen containing ozone/ N_2O_4 in traces through destructor. Cryostat of Julabo make provides the means of obtaining cryostat fluid at -70°C as coolant to realize sub zero temperature in reactors and collectors. The control module includes an instrument panel for process monitoring and remote operation. The material of construction of all the metal parts of plant (except the scrubber column and the scrubber chamber made of glass) and inter-connecting tubings is SS 316L. Teflon tubings are used for column internals. Cold insulation using polyurethane foam (PUF) and aluminium sheet is used for coolers, chiller-cum-collectors, and interconnecting tubing. Process flow diagram of the installation is shown in flow chart (Plate 1).

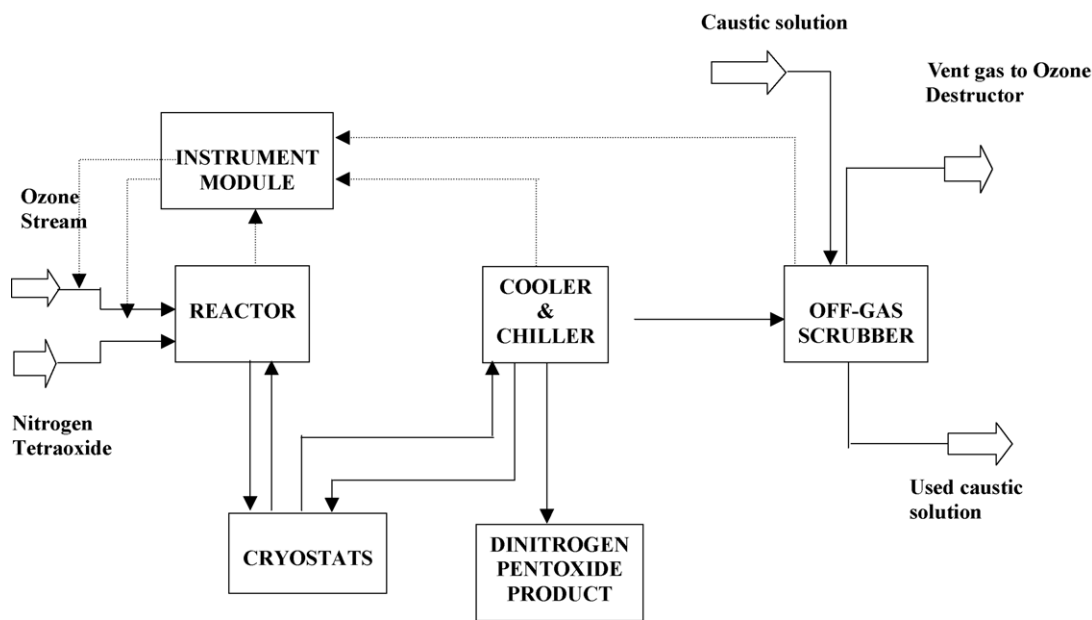
2.2. Materials for N_2O_5 synthesis

Ozone was generated from ozone generator of SORBIOS, GmbH, Germany make. It is capable of producing O_3 at the level of 200 g/h with oxygen flow rate of 1.5–2.0 m^3 . The operating pressure selected was 6–9 psi though the system has maximum limit of 20 psi. Ozone concentration in the gas stream was expected to be 8–10 mol% in oxygen. Commercially available ultra high pure (UHP) grade oxygen was used as feed for the generation of ozone. The liquefied N_2O_4 (purity 99.6%) was obtained from Hindustan Organics Corporation (HOC) in 1–3 L capacity cylinders and was used as such without further purification.

2.3. Dinitrogen pentoxide synthesis at HEMRL

N_2O_4 from its cylinder was led through heating and expanding assembly into the reactors (maintained at 30°C) along with ozone (7–8%) obtained from the ozone generator at pre-selected rates controlled by regulators to realize specified molar ratio. The two gases were allowed to mix in the reactor beyond the mixing nozzle. The rapid reaction resulted in rise in temperature, which was monitored through the thermocouples provided though out the length of the reactor. The reactors are designed by considering heat of reaction of $26.5 \text{ kcal mol}^{-1}$ to ensure that the temperature does not exceed beyond 60°C . Chilled methanol was circulated in the jacket of the reactor to maintain the desired temperature. Gaseous product containing N_2O_5 to the tune of 9% in bulk oxygen was led to the cooler and temperature was maintained to $0\text{--}5^\circ\text{C}$. They were further led to chiller-cum-condenser maintained at -60°C . N_2O_5 was deposited on the inner cooling surface of the unit. Uncondensed gases were led to the lower end of cold finger condenser and then to scrubber.

The product was characterized by UV (GBC: Cintra-10 E) and IR (Perkin-Elmer FTIR-1600 spectrophotometer) spectrum. DSC study was carried out on Perkin-Elmer DSC-7 instrument operating at a temperature rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Plate 1. Schematic diagram of N_2O_5 plant.

2.4. Feasibility of nitration by synthesized N_2O_5

In order to establish the feasibility of N_2O_5 aided nitration simple precursors were selected. A known quantity of benzene was taken in a three necked flask and allowed to cool to $-20^\circ C$ over a cryostat. The dinitrogen pentoxide dissolved in dichloromethane was added drop wise to the benzene over a period of 10–15 min. The reaction was allowed to proceed for additional 30 min at $-20^\circ C$. The reaction mixture was allowed to reach room temperature and stirred for 1 h under nitrogen atmosphere. Subsequently, it was poured onto crushed ice and neutralized with saturated sodium bicarbonate solution (pH 6.5–7.0). The aqueous and organic layers were separated. The organic layer was dried over anhydrous sodium sulphate and filtered. The dichloromethane was removed under vacuum and the product obtained was characterized. Yield: 78 %; nitrobenzene: IR (cm^{-1}) 3084, 2978, 1600, 1524, 1454, 1346, 1176, 1110, 1036, 918, 840, 790, 734, 532, 462.

2.5. Precursors of CL-20

All chemicals and solvents needed for the synthesis of precursors of CL-20 were of more than 98% purity and were used as such without further purification. Pd/C was obtained from Lancaster. The precursors of CL-20 were namely hexabenzyl isowurtzitane (HBIW), 4,10-dibenzyl-2,6,8,12-tetraacetyl hexaazatetracyclo [5,5,0,0^{3,11}0^{5,9}] dodecane (TADBIW), 2,6,8,12-tetraacetylhexaazatetracyclo [5,5,0,0^{3,11}0^{5,9}] dodecane (TAIW) and 4,10-dinitroso-2,6,8,12-tetraacetylhexaazatetracyclo [5,5,0,0^{3,11}0^{5,9}]dodecane (TADNIW) synthesized as per reported methods and characterized (Table 5) by elemental analysis as well as spectroscopic technique.

TG-FTIR of the well-characterized precursors and nitrated product was undertaken on simultaneous thermogravimetry–differential temperature analysis (TG/SDTA-Mettler Toledo 8551) in conjunction with FTIR of Bruker make (Model-55).

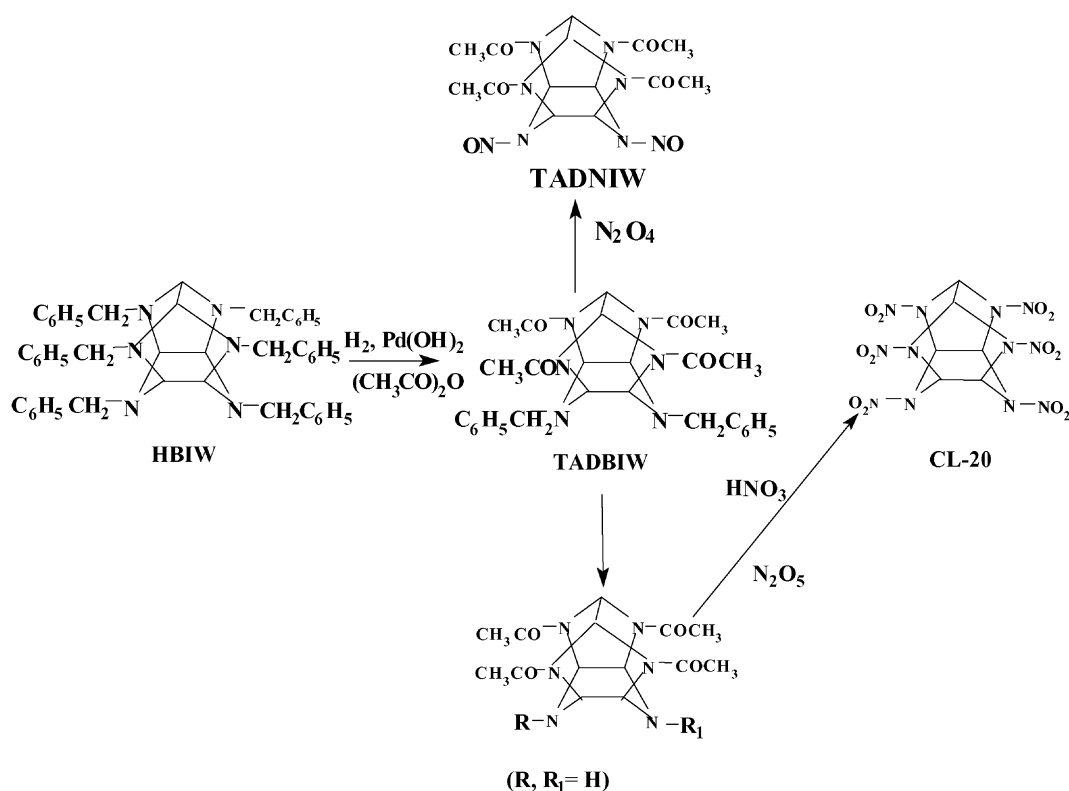
2.5.1. Nitration of HBIW, TADBIW and TAIW using N_2O_5

HBIW/TADBIW/TAIW (3.5 g/2.6 g/1.6 g, 0.005 mol) was dissolved in dichloromethane ($10\text{--}20\text{ cm}^3$) in a round bottom flask. The flask was fitted with a guard tube and nitrogen purging assembly. The contents of the flask were cooled to $-20^\circ C$. Dinitrogen pentoxide (4.5 g) was dissolved in 10 cm^3 of dichloromethane chilled to $-20^\circ C$ and added to the precursor solution in round bottom flask. The contents of the flask were kept at $-20^\circ C$ for 30 min, and then temperature was allowed to increase to room temperature. The reaction mixture was poured on the crushed ice. The organic layer was separated and washed with sodium bicarbonate solution. It was dried over magnesium sulphate and the excess of dichloromethane was evaporated under vacuum (Scheme 1).

In the next set of experiment, HBIW/TADBIW/TAIW (3.5 g/2.6 g/1.6 g, 0.005 mol) was added to dinitrogen pentoxide (5 g) dissolved in 98% nitric acid (10 cm^3) cooled down to $-20^\circ C$ in a round bottom flask fitted with a guard tube and nitrogen purging assembly. The contents of the flask was maintained at $-20^\circ C$ for 2 h and then allowed to reach to room temperature. The reaction mixture was poured on crushed ice. The solid precipitate was dissolved in ethyl acetate and neutralized with sodium bicarbonate solution. The organic layer was separated and concentrated. The concentrated liquid obtained from both the routes was chromatographed through silica gel (60–120 mesh) column using

Table 5
Characterization data of HBIW, TADBIW, TAIW and TADNIW

HBIW:	MP (°C): 154–155 C ₄₈ H ₄₈ N ₆ —C: 81.49, H: 7.01, N: 11.78 IR (cm ⁻¹): 3388, 3024, 2832, 1598, 1490, 1450, 1340, 1170, 1064, 984, 832 ¹ H NMR (δ): 7.20–7.24 (s, ph) 3.57 (s, 2H, -CH-), 4.03 (s, 4H, -CH-), 4.09 (s, 8H, -CH ₂ -), 4.16 (s, 4H, CH ₂ -) Mass: 710 (M + 1), 708 (M+), 617 (100), 525 (15), 435 (20), 230 (24), 91 (30)
TADBIW:	MP (°C): 321–325 Elemental analysis: C ₂₈ H ₃₂ N ₆ O ₄ —C: 64.91, H: 7.42, N: 16.12 IR (cm ⁻¹): 2926, 2866, 1690, 1654, 1408, 1358, 1306, 1128, 1078, 990, 776 ¹ H NMR (δ): 7.25–7.60 (m, 10H), 6.8 (br, 2H, CH), 5.4–5.8 (br, 4H, CH), 4.2–4.4 (br, 4H, CH ₂) 2.0–2.6 (br, m, 12H, CH ₃) Mass: 517 (M + 1), 516 (M+), 475, 382, 363, 292, 171, 111, 91 (100%), 69
TAIW:	MP (°C): 322 Elemental analysis (%): C ₁₄ H ₂₀ N ₆ O ₄ —C: 53.6, H: 5.4, N: 23.9 IR (cm ⁻¹): 3368, 3046, 1660, 1400, 1296, 1254, 1160, 1108, 1018, 974, 908, 800, 710 ¹ H NMR (δ): 1.96(s, 6H, -COCH ₃), 2.0 (6H, COCH ₃), 5.29(2H), 5.50(2H), 6.4(2H)
TADNIW:	MP (°C) 290–295 °C (dec.) IR (cm ⁻¹): 2984, 1728, 1534, 1486, 1414, 1352, 1286, 1136, 924, 856, 794, 722, 690 As TADNIW could not be obtained in good yield, its reaction with N ₂ O ₅ was not pursued to obtain CL-20



Scheme 1. Synthesis of CL-20.

mixture of ethyl acetate and hexane as eluent. The fractions were concentrated under vacuum.

3. Results and discussions

3.1. Synthesis and characterization of N₂O₅

As gaseous N₂O₄ is about 2.5 times denser than the ozone, the N₂O₅ reactor is designed to avoid their demixing. It was achieved by minimizing dead space in the N₂O₄ line and ensuring its venturi mixing with O₃ at the reactor inlet as

well as use of baffles along the entire length of the reactor to avoid formation of pockets of unmixed N₂O₄/O₃. The poor heat transfer characteristics of the gas necessitated the use of a series of coolers and chillers for the collection of N₂O₅ in the solid form (schematic diagram of plant is given in flow chart Plate 1). A scrapper was integrated as component of chiller-cum-collector to take care of poorer heat transfer during deposition of solid N₂O₅. A series of cold-finger condensers immersed in a cryostat was also found a viable collector with simple design features. Excess flow of ozone was avoided as it may alter the dew point of product gas resulting in difficulties in condensation/deposition of N₂O₅.

Table 6
Reaction parameters of N_2O_5 synthesis

O_3 and N_2O_4 feed pressure (kg/cm^3)	O_3 Flow rate (FR) (g/h)	N_2O_4 FR (g/h)	Temperature ($^{\circ}C$)	Time (h)	Yield (%)
0.55	170–190	50–70	40–50	1–1.5	48
0.55	170–190	50–70	50–60	1–1.5	55
0.55	170–190	50–70	60–70	1–1.5	68
0.55	170–190	50–70	70–80	1–1.5	50
0.55	170–190	100–120	60–70	1–1.5	28
0.55	170–190	150–170	60–70	1–1.5	23
0.55	140–160	50–70	60–70	1–1.5	40
0.55	90–120	50–70	60–70	1–1.5	34

A series of experiments was carried out in the lab scale plant to establish reaction parameters to synthesize N_2O_5 and the optimized parameters are given in Table 6.

It appears that 3:1 ratio of flow rate of $O_3:N_2O_4$ and their reaction time of 1–1.5 h result in reasonable yield of N_2O_5 in the reaction temperature range of 50–70 $^{\circ}C$. The N_2O_5 formed was collected at $-70^{\circ}C$. The IR spectra of N_2O_5 exhibited stretching frequencies at 1428, 1266, 1249, 1206, 1044, 822, 750, 546 and 454 cm^{-1} . The N–O–N stretching frequency was observed at 1044 cm^{-1} . The UV of N_2O_5 showed characteristic absorption bands at 204, 213, 258 nm ($\pi \rightarrow \pi^*$) 378 and 384 nm ($n \rightarrow \pi^*$) transitions. The data obtained is in agreement with the literature data [62]. DSC of N_2O_5 showed minor exothermicity with maxima at 32 $^{\circ}C$ suggesting that it undergoes sublimation accompanied with decomposition.

3.2. Nitration of CL-20 precursors

The conversion of HBIW directly to CL-20 is one of the major challenges faced by the HEMs community. The direct

nitrolysis of HBIW to CL-20 is well reported to be unsuccessful due to competing nitration of phenyl rings [114]. In the present study, the nitration of HBIW by dinitrogen pentoxide enriched nitric acid as well as dinitrogen pentoxide dissolved in dichloromethane was attempted. The product could not be isolated on nitration of HBIW, TADBIW and TAIW in organic solvent. Reaction of HBIW with N_2O_5 enriched HNO_3 led to the formation of low melting compound. The IR spectrum of the product indicated the cleavage of the cage structure. Subsequently, well reported precursor TADBIW obtained by reductive debenylation of HBIW was subjected to nitration by DNPO. Nitration of TADBIW in N_2O_5 enriched HNO_3 yielded a product, which could be resolved into three components by thin layer chromatography (TLC). The components were separated on column. IR revealed the presence of both C- NO_2 and N- NO_2 suggesting that nitration of both isowurzitanene nitrogen as well as phenyl ring [114] Consequently, completely debenzylated precursor TAIW was selected for N_2O_5 nitration. The nitration of TAIW in solvent medium did not yield the isolable products as in the case of HBIW and TADBIW. However, the nitration

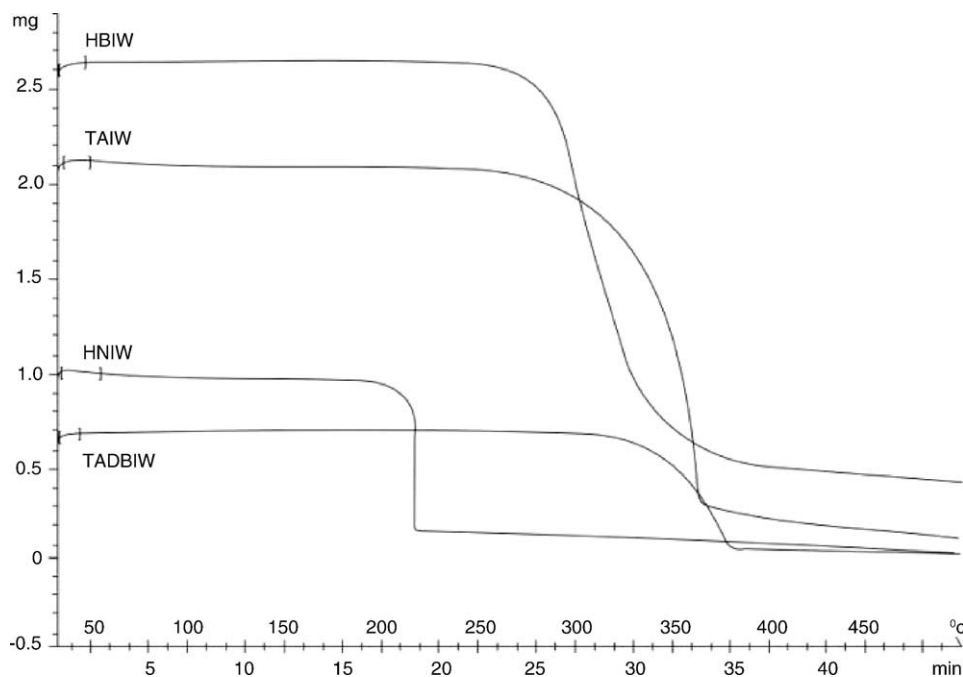


Fig. 1. TG of HBIW, TAIW, HNIW and TADBIW.

in N_2O_5 enriched nitric acid led to the formation of white amorphous material, which was resolved by column chromatography into three components.

Decomposition temperature and elemental analysis as well as IR and NMR of the first component matches with the reported data for CL-20 confirming its formation

CL-20	MP ($^{\circ}C$): 226–238 (dec.) Elemental analysis (%) $C_6H_6N_{12}O_{12}$ —C: 16.45, H: 1.38, N: 38.36 IR (cm^{-1}): 3028, 2882, 1592, 1510, 1282, 1044, 962, 872, 750, 714, 666, 568 1H NMR (δ): 8.33, 8.18 Mass (%): 439 ($M + 1.30$), 347(26), 301(28), 255(14), 209(14) The other two components also showed the decomposition temperature above 220 $^{\circ}C$. It appears that two components are partially nitrated isowurtzitane products.
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The CL-20 and its precursors (TADBIW and TAIW, HBIW) were also subjected to hyphenated TG-FTIR studies to get an insight into their decomposition pathways. The TG of HBIW (Fig. 1) indicated the single step endothermic decomposition process with weight loss of 91% in the temperature range of 260–360 $^{\circ}C$. TADBIW and TAIW underwent single step endothermic decomposition in the temperature range of 280–385 $^{\circ}C$ with a weight loss of 88 and 85%, respectively (Fig. 1). The FTIR of gaseous species evolved during TG of these compounds revealed the formation of similar decomposition products such as HCN (2358) and NH_3/NH_2CN (3264, 3612, 1696, 1520, 1464) providing supporting evidences (Fig. 2). FTIR of gaseous decomposition products of TADBIW and TAIW (Figs. 2 and 3) also revealed the presence of carbon monoxide and alkyl moiety (2824 cm^{-1}), which might be due to cleavage of acetyl

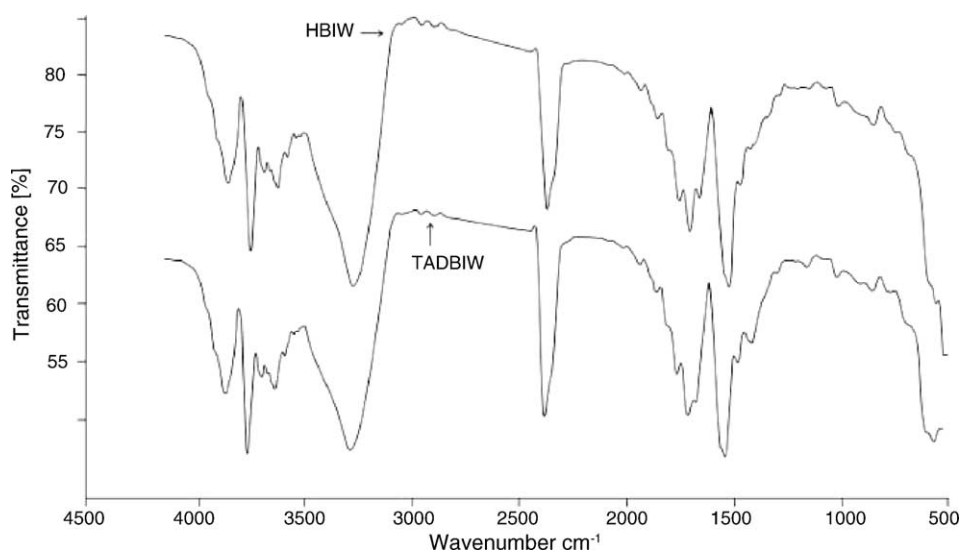


Fig. 2. TG-FTIR of HBIW and TADBIW.

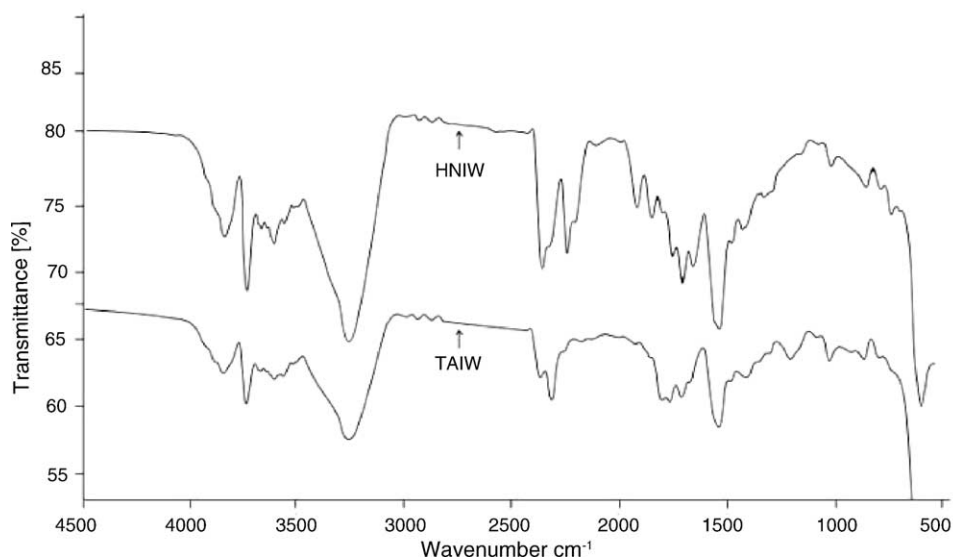


Fig. 3. TG-FTIR of HNIW and TAIW.

components. The TG–Mass of the TAIW also confirmed the evolution of NH_3 and CO as decomposition products along with IR inactive CO_2 (peaks at m/e 17, 28 and 44, respectively). The TG of CL-20 (Fig. 3) exhibited 72% weight loss in the temperature range of 220–300 °C followed by gradual decomposition of the residue accompanied with 15% weight loss in the temperature region of 306–506 °C as reported earlier [103,106]. The gaseous products of decomposition of CL-20 (Fig. 3) were found to be similar to those of TAIW suggesting the possibility of similar course of decomposition pathways, i.e. collapse of cage structure. The presence of NO_2 suggests the simultaneous cleavage of N-NO_2 of the cage structure. These findings are in line with those reported by Brill and co-worker [114].

4. Conclusions

This review brings out the potential of N_2O_5 as versatile nitrating agent for the synthesis of modern and novel HEMs. It discusses methods used for synthesis of N_2O_5 as well as its characterization and decomposition pattern. In view of the possibility of obtaining high purity N_2O_5 by interacting N_2O_4 with O_3 , a lab scale plant with modular design was established at HEMRL for the synthesis of N_2O_5 and reaction parameters were optimized. UV and IR spectra of the synthesized N_2O_5 were in close agreement with the reported value. The experiments on N_2O_5 aided nitration of CL-20 precursors brought out that TAIW is a material of choice for the synthesis of CL-20. TG-FTIR studies suggest that cleavage of cage structure is a major decomposition process in the precursor as well as CL-20 exhaustive studies need to be carried out to establish full fledged production of CL-20 by this approach as well as to pin point the mechanism of energy release of CL-20.

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