

## **STUDIES ON CL-20: THE MOST POWERFUL HIGH ENERGY MATERIAL**

*M. Geetha\**, *U. R. Nair*, *D. B. Sarwade*, *G. M. Gore*, *S. N. Asthana* and *H. Singh*

High Energy Materials Research Laboratory, Pune-411021, India

(Received December 24, 2001; in revised form July 15, 2002)

### **Abstract**

CL-20 is an attractive HEM having density ( $>2 \text{ g cm}^{-3}$ ) and velocity of detonation ( $9400 \text{ m s}^{-1}$ ) superior to HMX ( $1.9 \text{ g cm}^{-3}$  and  $9100 \text{ m s}^{-1}$ ). During this study, CL-20 was synthesized to establish viability of efficient synthesis method. The compound synthesized at HEMRL was characterized by FTIR,  $^1\text{H NMR}$  and elemental analysis. Thermal studies (dynamic DSC and isothermal TG) were undertaken to determine kinetic parameters and understand the decomposition patterns. An attempt is made to explain the mechanism of decomposition of CL-20 on the basis of the data obtained by the authors and findings of other researchers. The activation energy values obtained during this work by adopting various approaches are close to the values reported for N–NO<sub>2</sub> bond cleavage suggesting that it is global rate determining process rather than the collapse of cage structure. Mass spectra also provides evidences in this regard. Monitoring of decomposition products at high temperature supports these findings and brings out that NO<sub>2</sub> initiates secondary decomposition processes because of entrapment in cage structure.

**Keywords:** CL-20, high energy material, thermal analysis

### **Introduction**

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5,5,0,0<sup>3,11</sup>0<sup>5,9</sup>] dodecane or hexanitro hexaazaisowurtzitane (HNIW or CL-20) – a high energy material (HEM) with cage structure, is considered the most powerful explosive today. It is popularly known as CL-20. In view of its superior performance, CL-20 is emerging as the next generation HEM. Its attributes of great interest are high density ( $>2 \text{ g cm}^{-3}$ ), due to cage structure, and positive heat of formation of the order of  $\sim 419 \text{ kJ mol}^{-1}$  because of typical structure features including ring strain [1]. CL-20 is envisaged to deliver 14 to 20% higher performance than HMX [2]. Its superior performance potential than HMX emanates not only from much higher  $\Delta H_f$  but also relatively superior oxygen balance. It was a laboratory curiosity for a long time. However, production technology breakthrough by Thiokol corporation, USA and SNPE, France [3] resulted in its emergence as a commercially viable su-

\* Author for correspondence: E-mail: hemsociety@rediff.mail.com

rior alternative to HMX. During this study, CL-20 synthesized and characterized in the laboratory was subjected to exhaustive thermal studies to get an insight of the decomposition processes and determine kinetic parameters. An attempt is made to compile the information available in literature and discuss the results obtained during this work in the light of the findings of other researchers.

## Experimental

### *Starting materials*

Glyoxal, benzyl amine, acetic anhydride, sulfolane used for synthesis were of Merk (98–99% purity). 10% Pd/C, nitronium tetrafluoroborate and nitrosonium tetrafluoroborate were obtained from Lancaster.

### *Characterization*

IR spectra were recorded on Perkin Elmer FTIR Model-1605 using KBr pellets.  $^1\text{H}$  NMR was recorded on Bruker-300 MHz with pulsed Fourier Transform system. Elemental analysis was carried out on elemental analyzer (CE Instrument model CHNO-1110). Mass spectra was recorded with JEOL – DS double focusing mass spectrometer at 70 eV applying Electron Impact [EI] technique. HPLC was carried out on the Perkin Elmer Instrument.

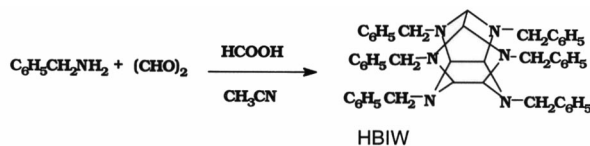
### *Thermal decomposition*

Thermal analysis at different heating rates was carried out using DSC (Perkin Elmer) and STA (Mettler Toledo) in  $\text{N}_2$  atmosphere.

## Results and discussion

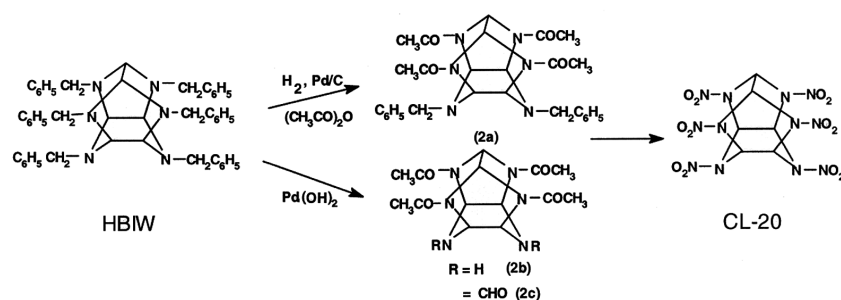
### *Synthesis*

The first step in HNIW synthesis [4] involves creation of basic cage structure through condensation of glyoxal with benzylamine leading to the formation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo [5,5,0,0<sup>5,9</sup>,0<sup>3,11</sup>] dodecane (HBIW) (Scheme 1). Conversion of HBIW to CL-20 poses major challenge.



**Scheme 1** Synthesis of HBIW

Direct debenzoylation of HBIW by nitrolysis is unsuccessful due to competing nitration of phenyl rings [5]. Thereby, debenzoylation precedes the nitration as a necessary step. The removal of N-benzyl groups is usually achieved by catalytic hydrogenation. However hexaaza isowurtzitane itself being unstable, it is necessary that six secondary amine groups be protected during the transformations. The reductive debenzoylation of HBIW under a wide variety of hydrogenation conditions to get tetraacetyl derivative of isowurtzitane (Scheme 2) with palladium catalyst has been investigated by various researchers [6–8]. Intermediates are converted to CL-20 by reacting with nitronium salt ( $\text{NOBF}_4$ ) [9] followed by nitronium salt [ $\text{NO}_2\text{BF}_4$ ]. 98%  $\text{HNO}_3$  also produces CL-20 at high temperature [10].

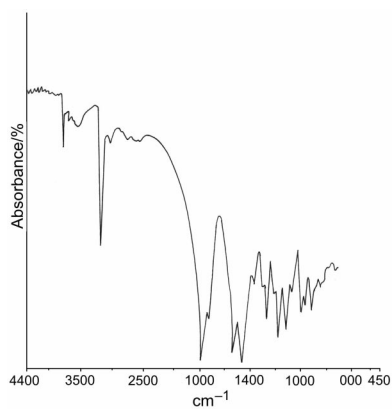
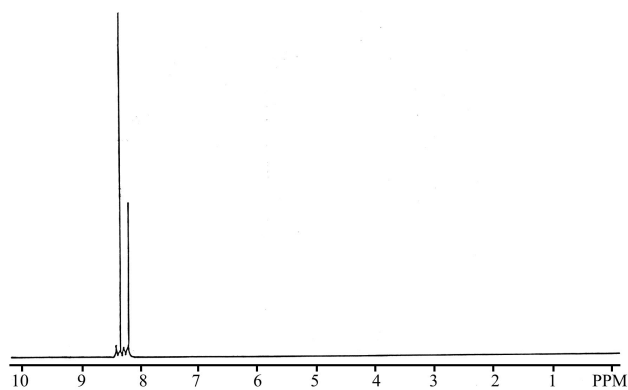
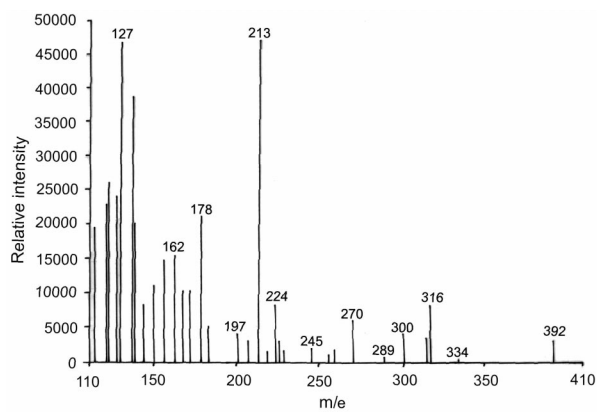


Scheme 2 Debenzoylation of HBIW followed by nitration

The synthesis work carried out in this lab also suggests that reductive [9] debenzoylation in conjunction with acetylation is a viable method to obtain an intermediate akin to nitration.  $\text{NOBF}_4$  and  $\text{NO}_2\text{BF}_4$  combination was used for the nitration of the precursor in preference to 98%  $\text{HNO}_3$  during this work, because the requirement of high temperature renders the later process hazard prone. It was observed that high purity compound could be obtained by this method. The purity of the compound was found to be >95% with HPLC. A mixture of acetonitrile, water and phosphoric acid was selected as eluent as recommended by Jacob *et al.* [11]. Relatively cost effective  $\text{N}_2\text{O}_4$  based nitrating agent combination was also investigated [9].

#### Characterization

FTIR gives peaks at 1600 and 1330  $\text{cm}^{-1}$  for  $\text{N}-\text{NO}_2$  and 3020  $\text{cm}^{-1}$  for  $(-\text{CH}-\text{str})$ .  $^1\text{H}$  NMR gives two signals at 8.4 $\delta$  (corresponding to 4H) and 8.2 $\delta$  (corresponding to 2H).  $^{13}\text{C}$  NMR shows singlets at  $\delta$ :75.0 and 72.1 respectively. Mass spectrum exhibits  $\text{M}^+-\text{NO}_2$  as fragment with highest  $m/e$  value. The  $\text{M}^+-3\text{NO}_2$  and  $\text{M}^+-6\text{NO}_2$  fragments were also observed in the EI model [12]. FTIR,  $^1\text{H}$  NMR and mass spectral patterns (Figs 1–3) of the CL-20 synthesized are concurrent with the reported values. C, H and N contents obtained by elemental analysis were close to theoretical values.

**Fig. 1** FTIR of CL-20**Fig. 2** <sup>1</sup>H NMR of CL-20**Fig. 3** Mass spectrum of CL-20 by (70 eV, EI)

### Thermal analysis

#### DSC

In DSC, single stage exothermic decomposition was observed at 233–246°C with the heat evolution of 883–945 J g<sup>-1</sup> at the heating rates of 10–25°C min<sup>-1</sup>. These temperatures are close to those reported by Wardle *et al.* for ε CL-20. The activation energy for exothermic decomposition computed by using ASTM standard method [13] (based on Kissinger correlation) was found to be 199.45 kJ mol<sup>-1</sup> (Table 1).

**Table 1** DSC data on CL-20 at various heating rates (Kissinger method)

Heating rate, β/ °C min <sup>-1</sup>	Decomposition T/K	-lnβ/T <sub>m</sub> <sup>2</sup>	k	A/min <sup>-1</sup>	Activation energy/kJ mol <sup>-1</sup>
10	511.5	10.176	1.0391		
15	512.5	9.766	0.9483	1.215·10 <sup>20</sup>	199.45
20	517	9.5003	1.5614		
25	519	9.284	1.8667		

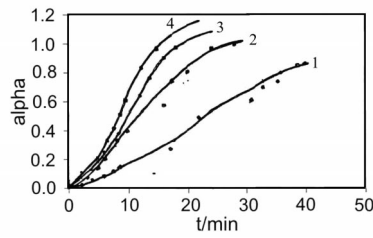
#### TG data: Isothermal kinetics

The kinetics of the decomposition of CL-20 were determined under isothermal conditions in the temperature range of 210–220°C (in nitrogen atmosphere). Collected data was analyzed by following ways.

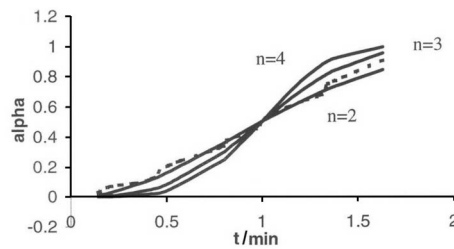
(i) The plot of α vs. t is sigmoid (Fig. 4) suggesting the Avrami–Erofeev rate expression. All the experimental α vs. t curves were converted to reduced-time scale ( $t_{red}/t_{0.5}$ ) where  $t_{0.5}$  is the time at each temperature at which α=0.5 [14]. Comparison of this experimental curve at 220°C with the theoretical reduced time curves per the Avrami–Erofeev model  $\alpha=1-\exp(-k_{0.5}t_{red})^n$  where  $k_{0.5}=[-\ln(0.5)]^{1/n}$ , (Fig. 5) confirms that accelerating period is close to n=2, while decelerating period best fitted when n=2 and 3. Accordingly rate constants  $k_{n2}$ ,  $k_{n2.5}$  for each temperature were evaluated for 0.05<α<0.5 (for acceleratory) and 0.5<α<0.95 (for deacceleratory) respectively. Arrhenius plot then gave the apparent  $E_a$  and frequency factor A (Table 2).

**Table 2** Apparent Arrhenius parameters for the thermal decomposition of CL-20 (483–493 K)

	Activation energy/		lnA/min <sup>-1</sup>
	kJ mol <sup>-1</sup>	kcal mol <sup>-1</sup>	
Acceleratory period n=2 (0.05<α<0.5)	224.93	53.55	22.25
Deacceleratory period n=2.5 (0.5<α<0.95)	247.13	58.84	25.15



**Fig. 4** Plot of  $\alpha$  vs.  $t$  at different temperatures; 1 – 210°C; 2 – 215°C; 3 – 218°C; 4 – 220°C



**Fig. 5** Experimental (---) and theoretical (Avrami–Erofeev) reduced time curve of CL-20

**Table 3** Correlation coefficient  $R$  obtained for various  $F(\alpha)$  by isothermal TG

No.	$F(\alpha)$	Isothermal temperatures/°C			
		210	215	218	210
1	$\alpha$	0.9529	0.9278	0.9306	0.9320
2	$-\ln(1-\alpha)$	0.9899	0.9909	0.9949	0.9847
3	$3/2[1-(1-\alpha)^{2/3}]$	0.9821	0.9913	0.9880	0.9735
4	$1/2[1-(1-\alpha)^{1/2}]$	0.9766	0.9848	0.9797	0.9656
5	$1/3[1-(1-\alpha)^{1/3}]$	0.9699	0.9724	0.9676	0.9561
6	$-[1-(1-\alpha)^{-1}]$	0.8738	0.7328	0.7580	0.8264
7	$[1-(1-\alpha)^{1/2}]$	0.9766	0.9848	0.9797	0.9656
8	$[1-(1-\alpha)^{1/3}]$	0.9699	0.9724	0.9676	0.9561
9	$[-\ln(1-\alpha)^{1/2}]$	0.9927	0.9848	0.9901	0.9838
10	$[-\ln(1-\alpha)^{1/3}]$	0.9943	0.9956	0.9971	0.9938
11	$[-\ln(1-\alpha)^{1/4}]$	0.9918	0.9972	0.9964	0.9969
12	$[1-\alpha][\ln(1-\alpha)]+\alpha$	0.9058	0.9508	0.6247	0.8963
13	$[1-2/3\alpha]-[1-\alpha]^{2/3}$	0.8942	0.9368	0.9073	0.8821
14	$[1-(1-\alpha)^{1/3}]^2$	0.8698	0.9015	0.8681	0.8522

(ii) Best linearization is achieved by plotting  $f(\alpha)$  vs.  $t$  using various expressions (Table 3) with the aid of a computer program. The best linearity with a correlation co-

efficient of 0.9972 was obtained for Avrami–Erofeev equation  $[-\ln(1-\alpha)^{1/4}]$  up to 70% fraction. Close correlation was also observed with the Avrami–Erofeev equation  $[-\ln(1-\alpha)^{1/3}]$ . The rate constants obtained from the slope of the plots of these equations were substituted in Arrhenius relationship. The activation energy computed from slope of this plot was 225–234 kJ mol<sup>-1</sup> and  $A$  was  $7.691 \cdot 10^{23}$  s<sup>-1</sup>.

(iii) An alternative method for finding the activation energy of the reactions without fitting the results to a kinetic equation was also attempted as it is reported to be a valuable means for obtaining the activation energy for a reaction when the order

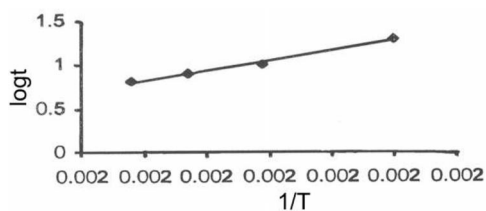


Fig. 6 Plot of  $\log t$  vs.  $1/T$  at  $\alpha$  range 20–60%

is unknown over a finite range of decomposition [15]. Let the rate equation be of the general form  $F(\alpha)=kt$ , where  $k$  is the rate constant. The relation obtained from experiments is  $F(\alpha_{n+1})-F(\alpha_n)=k(t_{n+1}-t_n)$  [ $\alpha_n, \alpha_{n+1}$  are the values of the fractional decomposition ( $\alpha$ ) at time  $t_n, t_{n+1}$ ]. At different temperatures  $F(\alpha_{n+1})-F(\alpha_n)=k'(t'_{n+1}-t'_n)=\text{constant}$ . It follows that the plot of  $\log(t_{n+1}-t_n)$  vs.  $T^{-1}$  is linear with a slope of  $E/2.303R$  (Fig. 6). With this approximation, the activation energy for thermal decomposition in  $\alpha$  range of 20–60% was found to be 209 kJ mol<sup>-1</sup>.

Xingzhong *et al.* [16] carried out studies on thermal stability of  $\epsilon$ -CL-20 using accelerating rate calorimeter (ARC) and obtained activation energy of decomposition ( $E_a$ ) of 189 kJ mol<sup>-1</sup>. Patil and Brill [17] reported activation energy of 153.6 kJ mol<sup>-1</sup> for global decomposition while Lobbecke *et al.* [18] reported  $E_a$  of  $171 \pm 6$  kJ mol<sup>-1</sup> for the non-catalytic processes and  $184 \pm 8$  kJ mol<sup>-1</sup> for catalytic process and observed that the commencement of heat release depends upon various factors like amount of sample, heating rate and composition of gaseous decomposition products. The treatment of DSC and TG data obtained during this work corresponds to  $E$  of  $209 \pm 25$  kJ mol<sup>-1</sup>.

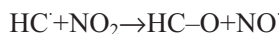
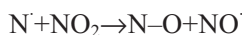
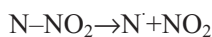
It can be inferred from activation energy values that the decomposition of CL-20 is basically dominated by hemolysis of N–NO<sub>2</sub> bond. Patil and Brill [17] have also proposed that N–N bond cleavage determines the global rate constant for decomposition at  $\sim 200^\circ\text{C}$ . Bouma *et al.* [19] also reached to similar conclusion. The supporting evidences are provided by mass spectral pattern obtained during this studies, where peaks corresponding to  $M^+-\text{NO}_2$ ,  $M^+-3\text{NO}_2$  and  $M^+-6\text{NO}_2$  were observed (Fig. 3).

Korsounskii *et al.* [20] carried out the analysis of the residue formed during decomposition at the heating rate of  $4^\circ\text{C min}^{-1}$  and proposed that it results from the elimination of  $5\text{NO}_2$  and undergoes exothermic decomposition beyond  $300^\circ\text{C}$ . Patil and Brill [17] have also reported the formation of residue containing left out  $\text{NO}_2$

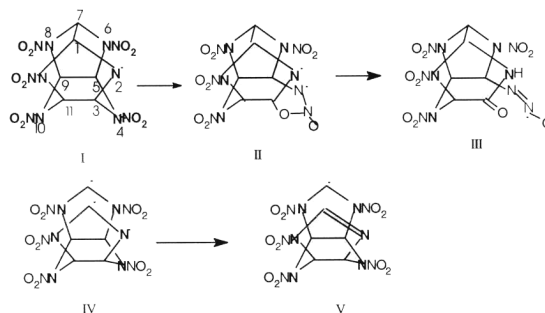
groups after main decomposition process. They found that it undergoes complete decomposition at temperatures greater than 700°C.

In order to get additional information, the sample was subjected to heating at elevated temperatures (180 to 240°C) and both the residue and the decomposition gases were subjected to FTIR study. No major change in IR spectra was observed for the samples up to 230°C and major decomposition appears to take place at 240°C. The selected frequencies and tentative assignments for FTIR of collected gaseous products of decomposition at 220°C show presence of NO and HCN, whereas FTIR of residue indicates presence of carbonyl, -NH and amide group. This brings out the possibility of rapid cleavage of N-NO<sub>2</sub> followed by secondary reactions. This aspect needs to be investigated in detail.

Patil and Brill [17] have proposed the formation of NO by the following pathway suggesting the relative importance of secondary reactions involving NO<sub>2</sub>.



It is opined that in case of HNIW, cage structure hinders the escape of decomposition products resulting in radical recombination in the backbone of CL-20. Stabilization of the C-N bond, subsequent to homolysis of N-NO<sub>2</sub> bond may be leading to residue formation unlike in case of RDX and HMX having two dimensional cyclic structure [21]. Possibilities of such recombination are also suggested by the presence of NH bond (3422 cm<sup>-1</sup>) in IR spectra of residue obtained during this work.



**Scheme 3** Decomposition pathways [17] of CL-20

Patil and Brill [17] have proposed a general reaction pathway on the basis of the data generated by them (Scheme 3). They assumed that the homolysis at N(2) results in the weakening of C(3) and N(4) bond (9I) facilitating the insertion of NO<sub>2</sub> unit with the creation of C-O-N bond (9II). The intermediate product could react in several ways leading the formation of N<sub>2</sub>O as well as carbonyl residue (9III). Parallely, C(1)-C(7) bond could cleave resulting in adjacent radical sites which may recombine to form C=N(9IV-V). HCN and CO are the common decomposition products of ni-



tramines, which may be formed by the decomposition of amide residue in the condensed phase, while HO-NO may result due to radical scavenging by NO<sub>2</sub>.

## Conclusions

The present study re-establishes that the debenylation via nitration is the most viable route for the synthesis of CL-20. However, attempts need to be continued to economize the production cost. Thermal studies suggest that N-NO<sub>2</sub> homolysis is the global rate determining step in decomposition of CL-20. However, cage structure appears to offer opportunities for rapid secondary reactions. The process of single stage rapid decomposition brings out efficient energy release capability of CL-20. In order to get direct visual evidence, the physical changes were closely monitored by hot stage microscopy and rapid decomposition processes accompanied with gasification were observed at 235°C in contrast to its precursors (devoid of N-NO<sub>2</sub> group). Moreover, the results obtained by the authors are more or less on the lines of those reported by other researchers despite different experimental condition/setup, are indicative of the overall validity of the proposed reaction pathways. However, exhaustive studies are needed to pin-point the mechanism of energy release of CL-20. Hyphenated thermal-spectral techniques and Coherent Antistroke Raman Spectra (CARS) may offer valuable information in this regard.

## References

- 1 R. B. Wardle, J. C. Hinshaw, P. Braithwaite, M. Rose, G. Johnston, R. Jones and K. Poush, 27<sup>th</sup> Intern. Ann. Conf. of ICT, 1996, p. 27.
- 2 R. L. Simpson, P. A. Urtiew, D. L. Ornellas, G. L. Moody, K. J. Scribner and D. M. Hoffman, Propellant, Explos. Pyrotech., 22 (1997) 249.
- 3 M. Golfier, H. Graindorge, Y. Longevialle and H. Mace, 29<sup>th</sup> Intern. Ann. Conf. of ICT, Karlsruhe, 1998, p. 3.
- 4 A. T. Nielsen, R. A. Nissan, D. J. Vanderah, C. L. Coon, R. D. Gilardi, C. F. George and J. F. Anduson, J. Org. Chem., 55 (1990) 1459.
- 5 A. J. Bellamy, Tetrahedron, 51 (1995) 4711.
- 6 (a) A. T. Nielsen, U.S. Department and Navy, U.S. Patent Office Application Case No. 70631, 24 June, 1987; U.S. Patent Application No. 253, 106, 30 Sep. 1988, U.S. Patent No. 5,693,794 C1540-554; CO7D259/00, 2 Dec. 1997; Chem. Abstr. 1998, 128, 36971t.  
(b) A. T. Nielsen, 'Synthesis and Caged Nitramine Explosives' presented at Joint Army, Navy, NASA, Air Force (JANNAF) Propulsion Meeting, San Diego, CA 17 Dec. 1987.
- 7 T. Kodama, M. Tojo and M. Ikeda, PCT Int. Appl. WO 9623792 (Cl, CO7D487/22), 8<sup>th</sup> Aug. 1996 CA; 125 (1996), 275920v.
- 8 R. B. Wardle and W. W. Edwards, PCT, Int. Appl. WO/97/20,785(Cl, CO6B25/34), 12 June, 1997 U.S. Appl. 568451, 7 Dec. 1995; Chem. Abstr., 127 (1997) 110983w.
- 9 A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. Moore, M. P. Nadler, R. A. Nissan and D. J. Vanderah, Tetrahedron, 54 (1998) 11793.

- 10 R. Surapanini, R. Damavarapu, R. A. Kumar and P. R. Dave, 'Process improvements in CL-20', 31<sup>st</sup> Int. Ann. Conf. of ICT, Karlsruhe 2000, p. 108.
- 11 G. Jacob, G. Lacroix and V. Destombes, 'Identification and analysis of impurities of HNIW', 31<sup>th</sup> Int. Ann. Conf. of ICT, Karlsruhe 2000, p. 106.
- 12 T. M. Klapotke, B. Krumm, G. Holl and M. Kaiser, 'Synthesis, characterization and Quantum Chemical Computations of Hexanitrohexaazaisowurtzitane', 30<sup>th</sup> Int. Ann. Conf. of ICT, Karlsruhe 1999, p. 120.
- 13 ASTM Standard test methods for Arrhenius kinetic constant for thermally unstable materials, 1982, Part 41, E698-79, p. 1012.
- 14 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, *J. Am. Ceram. Soc.*, 49 (1966) 379.
- 15 P. W. M. Jacobs and A. R. T. Kureishy, *J. Chem. Soc.*, 62 (1964) 4718.
- 16 W. Xingzhong, O. Yuxiang, C. Boron and F. Changgen, 'Determination of thermal stabilities of CL-20 and HMX using Accelerating Rate Calorimeter', Proc. of the 3<sup>rd</sup> Beijing Int. Symp. on Pyrotechn. and Expl., Beijing, China 1995, p. 520.
- 17 D. G. Patil and T. B. Brill, *Comb. and Flame*, 87 (1991) 145.
- 18 S. Lobbecke, M. A. Bohn, A. Pfeil and H. Krause, 'Thermal behaviour and stability of HNIW (CL-20)' 29<sup>th</sup> Int. Ann. Conf. of ICT, Karlsruhe 1998, p. 145.
- 19 R. H. B. Bouma, W. Duvalois, A. E. D. M. Van der Heijden and A. C. Van der Steen, 'Characterization of commercial grade CL-20: Morphology, crystal shape, sensitivity and shock initiation testing by Flyer Impact', 31<sup>th</sup> Int. Ann. Conf. of ICT, Karlsruhe 2000, p. 105.
- 20 B. Korsounskii, V. Nedelko, N. Chukanov, T. Larikova and F. Volk, 'Kinetics of Thermal Decomposition of Hexanitro Hexaaza Isowurtzitane' 30<sup>th</sup> Int. Ann. Conf. of ICT, Karlsruhe 1999, p. 64.
- 21 D. G. Patil and T. B. Brill, *Comb. and Flame*, 92 (1998) 456.