Spectro-thermal decomposition study of 1,4-dinitroglycoluril (DINGU)

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Abstract

Simultaneous thermal analysis and high temperature FTIR study of 1,4-dinitroglycoluril (DINGU) is reported. TG showed 90% weight loss in the temperature range 225–250 °C. Isothermal TG of DINGU showed about 70% weight loss in the temperature range 210–230 °C. Kinetic parameters evaluated using a computer program showed that α–t data are best described by the Avrami–Erofeev's equation for $n = 2$ with an activation energy of 165 kJ/mol. The kinetics of decomposition of DINGU was followed by studying N−H (3388 cm^{-1}), C=O (1770–1810 cm^{-1}) and NO_2 symmetric stretching (1565–1570 cm^{-1}) IR bands. All three bands showed loss of intensity with temperature and time. α–t data of decomposition with respect to NO_2 stretching was again best described by the Avrami–Erofeev's equation for $n = 2$. Gaseous decomposition products observed in the IR were N_2O, NO_2, CO_2, HCN and NO. PM3 and Hartree–Fock level calculations on various bond lengths, bond angles and dihedral angles were computed to support the analysis of decomposition study using TG and IR. The data showed that C−N and N−H bonds are much shorter than the N−N bonds, indicative of the weaker N−N bond and hence, the possibilities of rupture of the same bond preferentially. This paper also discusses the sensitivity and performance properties of DINGU.
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1. Introduction

Explosives belong to the category of the highly hazardous high energy materials (HEMs). 1,4-Dinitroglycoluril (DINGU) [1] is one of the important explosives, which has been of interest to the HEMs community in the recent past. This insensitive explosive is also a precursor to one of the most powerful explosive, viz. tetranitroglycoluril (TNGU) [2]. Various composite explosives with high explosion energy, good physico-chemical stability and extremely low vulnerability can be formulated using DINGU [3]. Thermal analysis of DINGU helps in assessing the decomposition pathways, and hence the management of risk arising out of unplanned detonation. It is also reported [3] that in case of

undesirable ignition of DINGU combustion occurs, but no deflagration to detonation happens. Therefore, DINGU is regarded as one of the potential ingredients for LOVA applications. DINGU is reported to have (LD_{50}) of 5000 mg/kg body weight in comparison to TNT and RDX (853 and 214 mg/kg body weight, respectively).

Low temperature thermolysis of high energy materials is an easy, controlled and reasonably accurate means of understanding the breakdown of a molecule under explosion conditions. Inferences from this technique have been proved in many cases accurate in predicting the decomposition pathway a priori [4]. The data from this technique is complemented by high temperature IR decomposition data. Isothermal decomposition was the preferred path. The samples were heated to temperatures just below the decomposition temperature of the substance in a diluent medium, kept at that temperature till decomposition occurred, and the stable decomposition products were then identified by IR spectroscopy. This technique is able to pinpoint the probable

decomposition pathway in terms of the preferences of bond breaking.

A combination of the low temperature thermolysis and high temperature IR studies is thus an excellent tool for the study of decomposition, which is precursor to combustion or detonation of high energy materials [5–7]. A method of corroborating the decomposition pathway is to theoretically compute the bond lengths, bond angles, etc. using ab initio quantum chemical calculations [8]. Insight into the weaker bonds, and thus the initiation and propagation centres of the decomposition reaction can thus be obtained, and can be used to simulate experimental conditions.

In this paper, the kinetics and mechanism of thermal decomposition of DINGU under isothermal conditions have been reported using simultaneous thermal analysis and high temperature IR spectroscopy. Ab initio quantum mechanical calculations have been carried out and the experimental results are supported by the computation data.

2. Experimental

2.1. Method

DINGU was prepared in gram quantities in the laboratory by a previously reported method [1]. The reagents used were of analytical grade. TG–DTA and isothermal TG were carried out on a Netzsch STA 409 thermal analyzer. About 10 mg of sample was used employing a heating rate of 10 °C/min and chart speed of 240 mm/h. IR spectra were recorded on a Perkin-Elmer spectrophotometer model 683 in the range of 4000–200 cm^{-1} in KBr matrix.

For the kinetic study by IR, the experimental techniques developed by Bent and Crawford [9] and Hisatsune and Hartman [10] were used with some modifications. These authors found that the KBr disc containing the sample when heated lost its transparency and regained it on re-pressing. The loss in transparency was due to the expansion of the pellet and also due to the trapped decomposition products (gases/intermediates). This method was used for trapping the gases/decomposition products in their study.

To avoid the above problems, the kinetics was followed by adopting the "loose mix" method. In this method, the sample and matrix material in the ratio 1:100 (about 30 mg sample and 3 g matrix material) were thoroughly mixed. Programmed heating and control achieved isothermal temperature and the same thermal cycle was repeated for a set of experiments. The temperature programming in each case was such that there was negligible reaction before attaining the desired isothermal temperature. A small sample (about 20 mg) of the mixture was withdrawn from the isothermal bath at regular intervals, quenched, smothered in the die, pelletized and scanned at ambient temperature. In this way, the kinetics determined was devoid of problems encountered by the earlier workers.

Kinetic parameters were obtained by isothermal IR study of NO$_2$ band. The thermal decomposition of DINGU by IR was studied in the temperature range 185–198 °C. The variation in intensity of the absorption band at 1565 cm^{-1} was used to monitor the decomposition. The absorbance of the sample when it attained the required temperature was taken on initial concentration. The ratio of the decrease in absorbance at any given time to that of initial absorbance gave 'α' (the mass fraction decomposed) versus 't' (time) curves obtained for the temperature range 185–198 °C. α versus t curves were sigmoid in nature, and they were used to evaluate the rate constants from various rate equations. The best fit for a correlation coefficient of 0.98 was obtained for the Avrami–Erofeev equation $n = 2$ for different temperatures studied. The plot of log k versus $1/T$ was found to be linear showing that it obeyed the Arrhenius equation. The data are shown in Fig. 8.

From the isothermal TG experiments in the temperature range 211–227 °C, the fraction 'α' that decomposed at any given time 't' was evaluated. The α–t curves thus obtained were sigmoid in nature. The α–t curves were analyzed using various kinetic model equations. The rate constants were evaluated from the slope of plot of the best fit equation, Avrami–Erofeev for $n = 2$ for the different temperatures studied. The best fit for a correlation coefficient of 0.98 was obtained for the Avrami–Erofeev equation $n = 2$ for different temperature studied. The plot of log k versus $1/T$ was found to be linear showing that it obeyed the Arrhenius equation. The data are shown in Fig. 9.

Evolved gas analysis by IR using a special gas cell with a furnace was designed for identifying the gases evolved during dynamic heating of the sample at a heating rate of 10 °C/min with 10 mg sample. The furnace consists of a brass cylinder with a hole of 1.6 cm diameter for inserting the test tube containing the sample. The heating of the furnace was programmed through a Stanton Redcroft temperature programmer and controller using a Cr–Al thermocouple. The sample (10 mg) was placed in the sample tube connected to IR gas cell. The IR gas cell was sealed with freshly prepared KBr discs. Before commencement of heating, a blank scan was done to ensure that there is no absorbance in any region. The IR spectra of gaseous molecules obtained were assigned by comparing with reported spectra.

Impact sensitivity was determined by the fall hammer method (2 kg drop weight), applying the standard Bruceton–Staircase test procedure. The height of 50% explosion probability (h_{50}) was determined by statistical analysis. Friction sensitivity was measured on a Julius Peters apparatus and is reported as the minimum weight under which the sample (10 mg) did not ignite/explode in five consecutive experiments.

2.2. Computation methods

Ab initio molecular orbital calculations have been carried out at the Hartree–Fock (HF) level using the 6-31G* basis set and using GAUSSIAN 94 program [11]. Two conformers,

viz. (a) planar and (b) the nitro groups perpendicular to the planar ring structure have been considered. Geometrical parameters such as bond lengths, bond angles and dihedral angles were computed. The performance of DINGU was predicted using a code named 'Linear Output Thermodynamic User-Friendly Software for Energetic Systems' (LOTUSES) [12].

3. Results and discussion

The simultaneous DTA–TG curve of DINGU decomposition is presented in Fig. 1. DTA showed an exotherm in the temperature range 225–250 °C, T_i at 225 °C and T_{max} at 235 °C, corresponding to a one-step, 90% weight loss in TG. The isothermal TG curve at 215 °C is shown in Fig. 2. α is the mass fraction decomposed at time 't'. Weight loss corresponding to 70% of the initial was observed in a single step. Curves of 'α', the fraction decomposed versus time 't' obtained from iso-TG curves in the temperature range 211–227 °C are shown in Fig. 3. The curves are sigmoid in nature especially at temperatures well below the dynamic decomposition temperature, obtained in the dynamic experiment.

IR spectra of DINGU samples decomposed at different temperatures are presented in Fig. 4. Peaks corresponding to gaseous products evolved are depicted in Fig. 5 and the isothermal IR spectra at different time intervals are presented in Fig. 6. Curves of α versus t obtained from isothermal IR spectra in the temperature range 185–198 °C are given in Fig. 7. The activation energy, E, corresponding to this fit was 160 kJ/mol (Fig. 8). The kinetic parameters derived from isothermal TG experiment were also found to best fit to the Avrami–Erofeev's equation for $n = 2$; the corresponding E
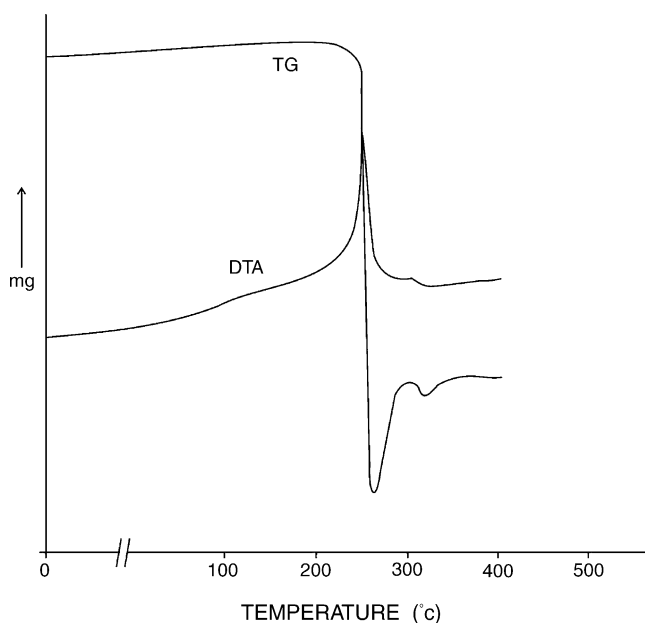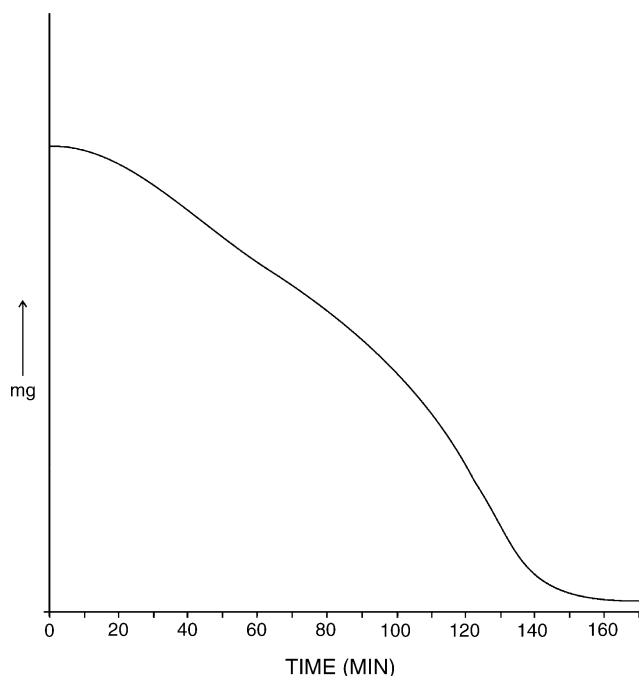

Fig. 2. Isothermal TG curve of DINGU at 215 °C.

was 165 kJ/mol (Fig. 9). The HF level optimized geometrical parameters like bond lengths, bond angles and dihedral angles are presented in Table 1. It can be seen from this table that the longest bond length ($1.539 \, m^{-10}$) observed was for C3–C5, which is akin to the X-ray crystal data ($1.542 \, m^{-10}$), and it may be attributed to the fact that these carbon atoms are attached to two electron withdrawing nitrogen atoms each of which, in turn, are connected to strong electron withdrawing NO_2 and carbonyl groups.
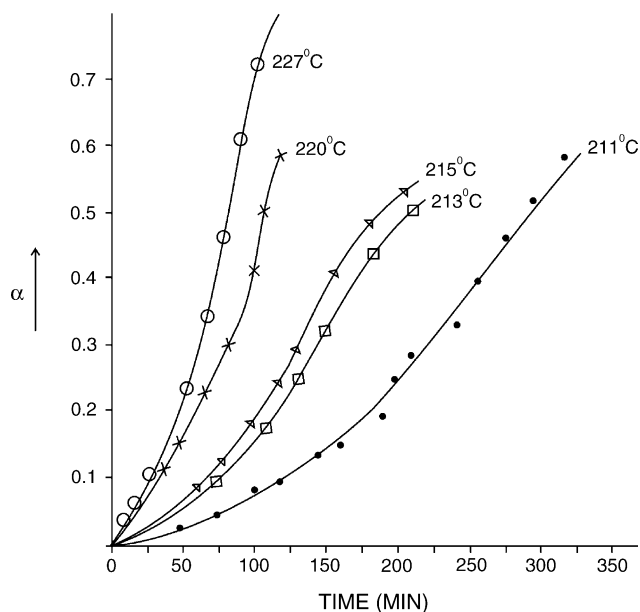

Fig. 1. Simultaneous DTA–TG curves of DINGU.

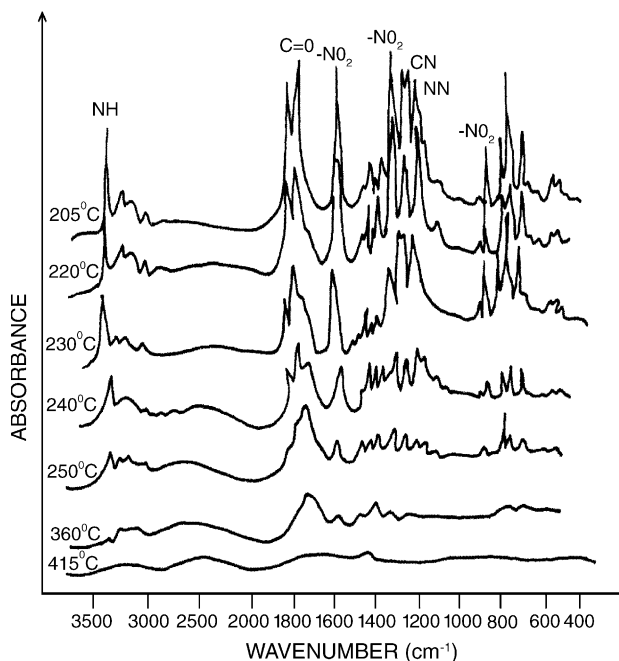Fig. 3. α–t plots from isothermal TG data.

Fig. 4. IR spectra of decomposed DINGU samples at different temperatures.

Single crystal structure of DINGU reveals two planes inclined at a dihedral angle of 117.5° with NO_2 groups in ex-position and N atoms of NO_2 groups in a plane [13]. Zeman [14–16] studied the non-autocatalyzed thermolysis of DINGU by TGA and DSC and reported E value in the range 209–218 kJ/mol.

N−N bond in DINGU though longer ($1.35\,m^{-10}$) [14] is to be considered stronger, for the IR absorption band for the N−N bond is observed at a higher frequency ($1180\,cm^{-1}$) as compared to the N−N bond in cyclotrimethylene trinitramine (RDX) ($1040\,cm^{-1}$). Compounds with long N−N bonds and high values of νNO_2 (asym), in general favour NO_2 liberation on fast thermolysis [4]. The tendency to form HONO (g) early
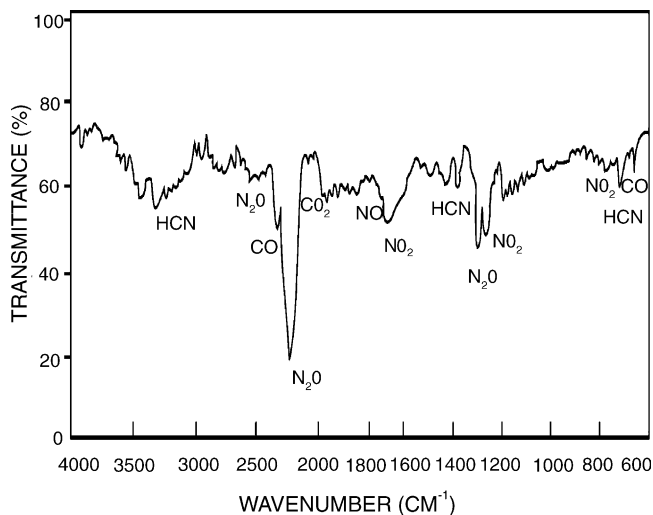
Fig. 5. Gaseous products obtained from IR experiments.
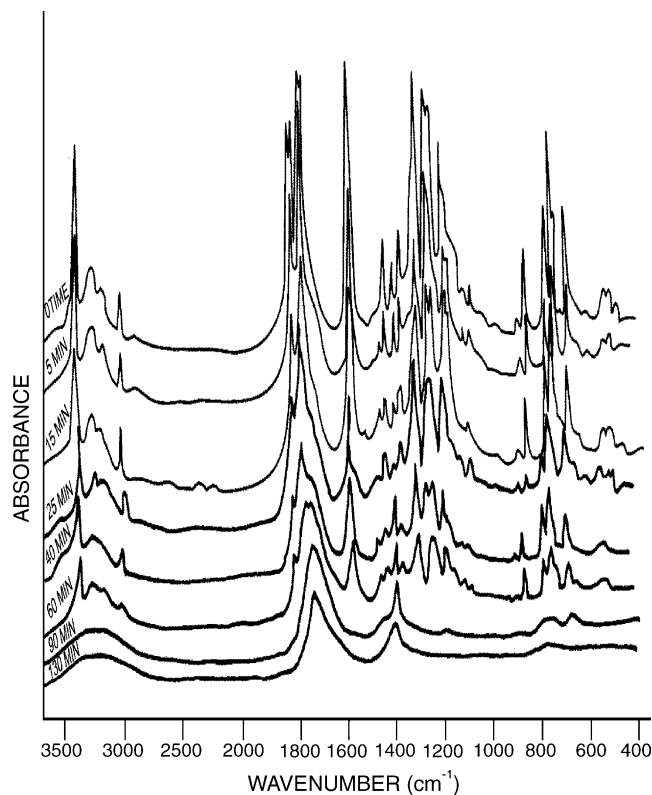
Fig. 6. Isothermal IR spectra at different time intervals of DINGU.

in the thermolysis depends on the H/NO_2 ratio in the parent secondary nitramine [17].

The average N−N bond distance of $1.375\,m^{-10}$ and average value of νNO_2 $1565\,cm^{-1}$ both favour NO_2 liberation.
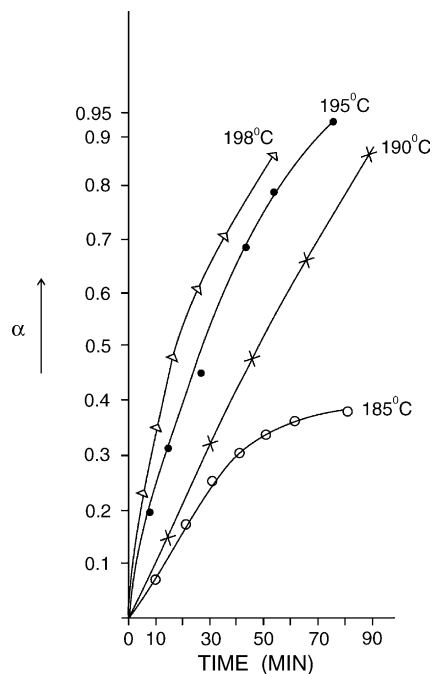

Fig. 7. α–t plots from isothermal IR data.
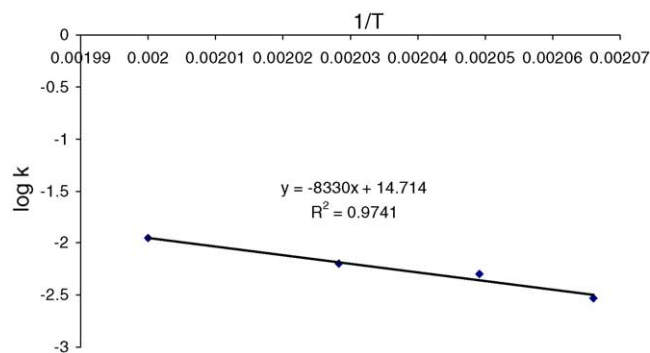
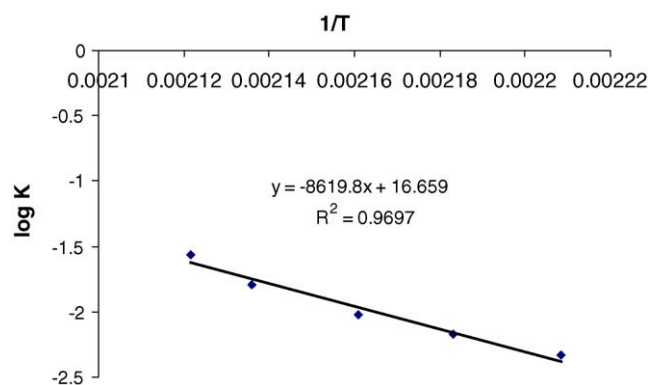Fig. 8. Arrhenius plot for thermal decomposition of DINGU by isothermal IR data.

Fig. 9. Arrhenius plot for thermal decomposition of DINGU by isothermal TG data.

But N_2O was found to be more dominant than NO_2 in fast thermolysis suggesting rather, the retention of N–N bond and the preferential ring fission leading to generation of N_2O and HNCO. The rate-determining step for the thermal decomposition of DINGU has been postulated to be N–H bond cleav-

age. HNCO generation indicates the fission of OC–NNO$_2$ as well as HC–NH bonds in the ring. Presence of NO_2 as a gaseous product suggests the cleavage of $>$N–NO$_2$ too. The rate determining N–H bond cleavage necessarily occurs through free radical attack on the N–H hydrogen atom, as –N–H is more reactive than the C–H in the ring. A free radical can be the one generated by the fission of N–NO$_2$ bond and the ring rupture.

The IR spectra recorded during the thermal decomposition as a function of time reveals intensity loss for all the bonds as expected, but the IR spectra vide Fig. 4 at 250 and 360 °C and vide Fig. 6 at 90 and 100 min are conspicuous for the near absence of NO_2 bands at 1570 and 1270 cm^{-1} and N–N band at 1180 cm^{-1}, with the retention of all other bands to a reasonable extend. This is direct evidence for the preferential N–NO$_2$ rupture as observed in similar systems [14]. The mechanism proposed for the thermal decomposition of DINGU is given in Scheme 1.

The activation energy obtained for the thermal decomposition in the present study, 165 kJ mol^{-1} is consistent with such a reaction mechanism. The bond dissociation energy for the N–H bond involved in the rate determining step is expected to be of the same order and consistent with the
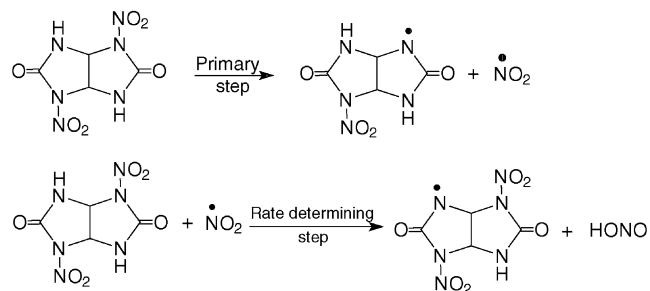
Scheme 1. Proposed thermal decomposition mechanism of DINGU.

Table 1
HF/6-31 G(d,p) optimized geometrical parameters of DINGU

Bond length (m^{-10})		Bond angle (°)		Dihedral angle (°)	
r(N$_2$C$_1$)	1.363	a(C$_1$N$_2$C$_3$)	114.8	d(N$_4$C$_3$N$_2$C$_1$)	92.9
r(C$_3$N$_2$)	1.419	a(N$_2$C$_3$N$_4$)	115.3	d(C$_5$C$_3$N$_2$C$_1$)	−16.4
r(N$_4$C$_3$)	1.460			d(C$_6$N$_4$C$_3$N$_2$)	−124.6
r(C$_5$C$_3$)	1.539	a(N$_4$C$_3$C$_5$)	100.8	d(N$_7$N$_4$C$_3$C$_5$)	−176.0
r(C$_6$N$_4$)	1.419	a(C$_6$N$_4$C$_3$)	113.5	d(N$_8$C$_5$C$_3$N$_4$)	16.7
r(N$_7$N$_4$)	1.359	a(N$_7$N$_4$C$_3$)	118.7	d(N$_9$C$_5$C$_3$N$_2$)	16.7
r(N$_8$C$_5$)	1.419	a(N$_8$C$_5$C$_3$)	103.9	d(N$_{10}$N$_9$C$_1$N$_2$)	165.7
r(N$_9$C$_1$)	1.419	a(N$_9$C$_1$N$_2$)	103.9	d(O$_{11}$C$_1$N$_9$C$_5$)	−174.5
r(N$_{10}$N$_9$)	1.359	a(N$_{10}$N$_9$C$_1$)	125.2	d(H$_{12}$N$_2$C$_1$O$_{11}$)	−12.5
r(O$_{11}$C$_1$)	1.176	a(O$_{11}$C$_1$N$_2$)	127.8	d(H$_{13}$C$_3$C$_5$N$_8$)	−101.3
r(H$_{12}$N$_2$)	0.995	a(H$_{12}$N$_2$C$_1$)	119.9	d(N$_{14}$C$_5$C$_3$N$_4$)	138.9
r(H$_{13}$C$_3$)	1.078	a(H$_{13}$C$_3$N$_2$)	112.0	d(H$_{15}$N$_8$C$_6$N$_4$)	168.2
r(H$_{14}$C$_5$)	1.078	a(H$_{14}$C$_5$N$_2$)	114.1	d(O$_{16}$C$_6$N$_4$N$_7$)	−13.6
r(H$_{15}$N$_8$)	0.995	a(H$_{15}$N$_8$C$_5$)	122.1	d(O$_{17}$C$_7$N$_4$C$_3$)	174.0
r(O$_{16}$C$_6$)	1.176	a(O$_{16}$C$_6$N$_4$)	128.2	d(O$_{18}$C$_7$N$_4$C$_6$)	−167.2
r(O$_{17}$C$_7$)	1.177	a(O$_{17}$C$_7$N$_4$)	118.9	d(O$_{19}$N$_{10}$N$_9$C$_5$)	−7.0
r(O$_{18}$C$_7$)	1.201	a(O$_{18}$C$_7$N$_4$)	114.2	d(O$_{20}$N$_{10}$N$_9$C$_5$)	174.0
r(O$_{10}$N$_{10}$)	1.201	a(O$_{19}$N$_{10}$N$_9$)	114.2		
r(O$_{20}$N$_{10}$)	1.177	a(O$_{20}$N$_{10}$N$_9$)	118.9	d(N$_4$C$_3$N$_2$C$_1$)	92.9

Table 2
Theoretically predicted explosive properties of DINGU

Sl number	Parameter	
1	Density (g/cm^3)	1.98
2	Heat of formation (k cal/mol)	−74
3	Oxygen balance (%)	−27.57
4	Velocity of detonation (m/s)	8000
5	Detonation pressure (k bar)	341
6	Detonation temperature (K)	4565
7	C_J pressure (GPa)	3225

quantum chemical calculation results obtained for DINGU by the HF method.

3.1. Sensitivity characteristics

The h_{50} for DINGU (particle size: 21 μm) was found to be 88 cm and the friction sensitivity to be 25 kg. The impact sensitivity obtained in the present investigation closely matches with the reported data (101 cm, Type 12 impact sensitivity set up) [18]. It is not possible to obtain a direct relationship between the sensitivity behavior of explosive materials and their chemical structure because of a complex interplay of physical and thermo chemical characteristics. However, the relative invulnerability of DINGU appears to be in agreement with its activation energy, which may be considered a measure of the probability of formation of hot spots.

3.2. Performance parameters

The theoretically predicted performance parameters are given in Table 2. It is clear from the table that DINGU exhibited velocity of detonation, 8000 m/s at theoretical maximum density. The reported [1] VOD of DINGU at a density of 1.867 g/cm^3 was found to be 7855 ± 17 m/s. The experimentally obtained velocity of DINGU:PU (95:5) in the present study was found to be 7162 m/s.

4. Conclusion

Kinetic parameters of thermal decomposition of DINGU were evaluated by following the asymmetric NO$_2$ stretching band in the IR and TG. The activation energy obtained for the decomposition of DINGU by both methods was almost identical and corresponds to the dissociation of the N−H bond, which is the rate-determining step in the decomposition. Quantum chemical calculations have thrown light on bond lengths and bond angles of the 1,4-DINGU isomer. The N−N bond seems to be the most vulnerable to dissociation; a

fact consistent with the primary step (breakage of N−N bond) in the decomposition mechanism of DINGU. The thermal analysis performed in this paper increases our understanding of the thermal decomposition mechanisms, which is the first step towards, improving safety in the manufacture and handling of this energetic material.

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