



Synthesis, characterization and thermal studies of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX or K-6)

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Abstract

2-Oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX or K-6), the most powerful energetic material among nitrorea explosives, has been prepared and scaled up at laboratory level. The identity and purity of the product are tested by elemental analysis, IR, NMR, mass and HPLC techniques. Thermal response and sensitivity experiments on K-6 are also described. The data on sensitivity shows that K-6 can be utilised practically only in phlegmatized form.

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1. Introduction

In the continuing search for superior energetic materials to offer improvements in both explosives and propellants formulations the successful utilization of monocyclic oligomeric nitamines like hexahydro-1,3,5-trinitro-S-triazine (RDX) [1] and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [2] and nitroaromatics like 2,4,6-trinitro toluene (TNT) [3], have been wide spread. However, owing to number of accidents involving initiation of munitions by impact/shock aboard ships, aircraft carriers and munitions train, there has been a need for the development of a conciliatory material having characteristics of insensitivity close to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and commensurate detonation performances.

Over the decades some of the products of the azaheterocyclic nitramine urea class have attained prominence to meet the requirements of increased stability and insensitivity coupled with high performance or a favourable compromise between these two

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properties [4–6]. The presence of nitrourea moiety in cyclic structure also ensures high density [7]. Amongst the compound investigated, 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX or K-6), structurally similar to RDX appears to be a better choice considering its several physical properties, good energy capability and thermal stability as well as the method of preparation from readily available cheap starting materials [8]. Mitchell et al. [8] has recently developed a cost effective synthetic route for the production of K-6 and reported one of the most inexpensive new explosive with 4% more energy than HMX. With this in mind, we have undertaken an effort to prepare, purify, characterize and scale up 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6) by the methods which are amenable to scale up as well as, have not afforded generality [9]. These synthetic methods have resulted in sufficient quantity of this material being available to allow a small scale evaluation studies. This study has further been extended to thermolysis behaviour of compound in order to understand the physico-chemical processes in the combustion of material for developing methods to modify formulations so as to achieve better ignition, combustion or sensitivity properties.

2. Experimental

2.1. Materials

All solvents used for the reactions were of analytical grade and used as such. Urea, hexamine, phosphorus penta oxide, formaldehyde solution (37%) and tertiary butyl amine were purchased from E-Merck, Germany. Acetic anhydride, polyphosphoric acid, and sulphuric acid were procured from S.D. Fine Chemicals. Fuming nitric acid was obtained from Ammunition Factory, Kirkee, Pune. Tertiary butyl amine was distilled prior to use.

2.2. Synthesis

2-Oxo-1,3,5-trinitro-1,3,5-triazacyclohexane has been prepared in our laboratory by following two different methods.

2.2.1. Method A

This method consists of two steps.

2.2.1.1. Synthesis of 2-oxo-1,3,5-triaza-5-tertiary butyl cyclohexane (TBT). A 2 l round bottom flask equipped with a thermometer, overhead stirrer and condenser, was immersed in an oil bath at $52 \pm 2^\circ\text{C}$. Urea (300 g, 5 mol) and formaldehyde (770 ml, 10 mol) were added and suspension was stirred. Immediately upon the dissolution of urea, tertiary butyl amine (530 ml, 5 mol) was added within 5 min. The stirring was continued for another 8 h. When the precipitation appears, stirring was continued for another 2–3 h. The reaction mixture is first cooled to room temperature, and then to ice temperature and stirred for 1 h. It was then filtered, washed with acetone to remove unreacted urea and dried to get the desired product with a yield of 53% (420 g). Melting point: 198°C . The purity of the

compound was examined by thin layer chromatography (TLC) and further confirmed by HPLC.

The compound has been synthesized in different batch sizes ranging from 20 to 300 g in the yield of 52–60%. The product obtained from different batches was identical and confirmed by spectral data and elemental analysis with those of authenticated samples.

2.2.1.2. Synthesis of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX or K-6) from TBT. A 2 l round bottom flask was charged with 90% fuming nitric acid (696 ml, 14.9 mol) and the temperature was maintained at 5 °C. TBT (106.8 g, 0.68 mol) was added in small portion with stirring and cooling (<10 °C) over 1 h. The resulting solution is cooled to <3 °C and acetic anhydride (696 ml, 7.36 mol) was slowly added over a period of 3 h with continuous stirring at 10–16 °C. The addition of acetic anhydride was discontinued if the temperature exceeds 16 °C. Product precipitated before all of the acetic anhydride had been added. The reaction mixture is stirred overnight with cooling provided with residual ice water. The resulting suspension is transferred to a 5 l beaker containing ice and water mixture. Cold water is used to rinse the residual product. The product is collected by filtration, washed with cold water to remove acid and finally dried to obtain crude Keto-RDX. Melting point: 177–179 °C, which is further crystallized by ethyl acetate to get white crystalline product, yield 20%, melting point: 181–182 °C.

2.2.2. Method B

Synthesis of Keto-RDX (K-6) involves three steps:

1. hydrolysis of hexamine,
2. nitration of urea,
3. condensation of steps 1 and 2 to yield Keto-RDX.

2.2.2.1. Hydrolysis of hexamine. Seven grams of hexamine was added within 10 min into a mixture of polyphosphoric acid (17.5 ml), nitric acid (5 ml) and phosphorus pentoxide (5.9 g) in a round bottom flask at 10 °C. After the addition, the mixture was kept at 15 °C for 20 min.

2.2.2.2. Nitration of urea. Twenty-two milliliter of concentrated sulphuric acid was taken in a flask for which the temperature was maintained below 10 °C by stirring following the addition of 8 g of urea. During the addition of urea, temperature was maintained at 25 °C and when the temperature was lowered to 0 °C, the nitric acid (9 ml) was fed drop-wise in 20 min. After the addition, the temperature of the reaction mixture was maintained at 10 °C for 40–50 min and further an additional quantity of 29 ml of nitric acid alongwith 9.8 g of P₂O₅ were added at 20 °C.

2.2.2.3. Condensation of steps 1 and 2. By the end of the operation as above, the mixture obtained from step 1 was fed at 10 °C into the mixture obtained from step 2 for a period of 20 min. The temperature of the combined mixture was maintained at 20 °C for 20–30 min. On lowering temperature and dilution with ice, Keto-RDX precipitated was filtered and

dried. Following the identical conditions several batches were made with proportionate mass ratio of the reactants. The yield of Keto-RDX varies from 42 to 68%.

However, this is not amenable to scale-up the product because of perplexity, high cost and inconvenience. The slight variation or inaccuracy of required amount of any component/reactant as well as reaction conditions can drastically affect the yield of K-6 or RDX either separately or combined. Following this method we could obtain highest yield 68% of monomolecular product K-6 alongwith 20% RDX.

2.3. Characterization

2.3.1. Structural aspects

IR Spectra were recorded on Perkin-Elmer, FTIR using KBr Pellets. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200 MHz Instrument with a pulsed Fourier Transform (FT) system at ambient temperature ($\sim 30^\circ\text{C}$). The chemical shifts (δ units) are reported in parts per million (ppm) downfield from tetramethyl silane (TMS) as internal standard. The UV spectrum (λ_{max} in nm) was measured in acetonitrile solvent. The absorption maxima were found at 196 and 234 nm, respectively. Mass spectrum was recorded on JEOL-DS double focussing mass spectrophotometer, at 70 eV using a direct insertion technique at a source temperature of about 200°C connected with an online data analysis system. Elemental analysis was carried out on Carlo Erba Elemental Analyser MOD, EA 1110.

2.3.2. Purity

Purity of the compound was established by thin layer chromatography (silica gel, “G”, Qualigens) with acetone–water (70:30) as the solvent system and also by high performance liquid chromatography (HPLC), with C8 μBp column, mobile phase comprise of acetonitrile–water (70:30) and acetonitrile–methanol–water (50:25:25) at a flow rate of 1 ml/min in isocratic mode with UV detector at 254 nm.

2.3.3. Thermal analysis

2.3.3.1. Simultaneous thermal analysis. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out simultaneously on Mettler Toledo Thermal Analyzer. The enthalpy change and mass change measurements were made using about 10 mg of samples at a heating rate of $10^\circ\text{C}/\text{min}$ in platinum–iridium thermocouples in the temperature range from 0 to 600°C in nitrogen air against equal amount of calcined alumina.

2.3.3.2. Differential scanning calorimeter (DSC). Perkin-Elmer DSC-7 was employed for DSC studies. A small amount of sample (2–3 mg) crimped in an aluminium pan was heated against crimped blank pan as reference at different heating rates, i.e. 5, 10, 15, 20 and $25^\circ\text{C}/\text{min}$. The amount of energy involved in the exothermal and endothermal change was obtained with delta softwares.

2.3.4. Explosive properties

Deflagration temperature was determined by heating 0.02 g of sample in a glass tube in Wood’s metal bath at a heating rate of $5^\circ\text{C}/\text{min}$ and temperature at which sample got

ignited was recorded as deflagration temperature [10]. Impact sensitivity was determined on impact machine using 2 kg drop weight according to Bruceton Stair Case Method [11] and friction sensitivity measurements were carried out by Julius Peter Apparatus by following the standard method [11].

Particle size was determined by Malvern Instrument SB 22 using methanol–water as dispersive medium.

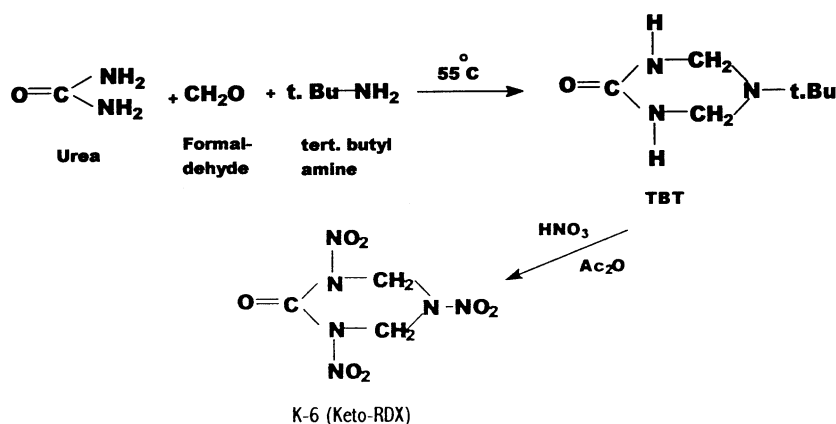
3. Results and discussion

3.1. Synthesis and structure

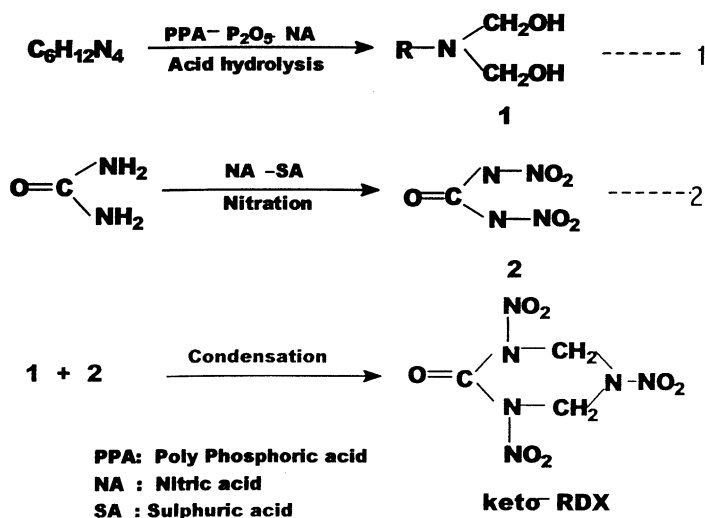
2-Oxo-1,3,5-trinitro-1,3,5-triazacyclohexane, popularly known as Keto-RDX or K-6, a cycloureanitramine compound and high energy explosive has been prepared by adopting the two different methods. Our first method involved the nitration of TBT which in turn was prepared by the reaction from an amine and urea by ring closure condensation with 37% formaldehyde in 52–60% yield (Scheme 1).

Although this method affords very low yield and needs to be repeated for sufficient quantity of the product for characterization and propellant formulation studies. We preferred this method for scaling up on considerations of safety, ready availability of low cost starting material and convenience of processing. This improved two step synthetic strategy has yielded in sufficient quantity of this material from different batch size reactions ranging from 6.7 to 106 g of TBT as starting material.

The alternative approach followed for the preparation of K-6 involves the acid hydrolysis, nitration and condensation of hexamine and urea separately in the polyphosphoric acid–nitric acid and nitric acid–sulphuric acid mixture (Scheme 2). The yield is good (~62%), but turned out to be more difficult owing to scattering yields and varying purity; depending on the optimum mass ratio of reaction components and conditions.



Scheme 1.



Scheme 2.

In addition, this method afforded both K-6 as well as its mixture with RDX (~20%), however the isolation of pure monomolecular product K-6 is very inconvenient and tedious.

Structure of TBT was confirmed by spectral data (IR, ^1H NMR and Mass) and elemental analysis. IR Spectrum shows, characteristic bands at 3226, 3058 and 1662 cm^{-1} corresponding to $>\text{NH}$, $-\text{CH}$ and $>\text{C}=\text{O}$ stretching frequencies. The ^1H NMR is in good agreement with the structure. One broad peak of NH appears at δ 6.24. The chemical shifts of methyl protons appear as a singlet at δ 1.15 and that of $-\text{CH}_2$ protons resonate as singlet at δ 4.1. The electron impact mass spectrum shows the molecular ion peak at m/z 157 along with other diagnostic peaks at m/z 142 ($M^+ - \text{CH}_3$), 139 ($M^+ - \text{H}_2\text{O}$), 100 ($M^+ - t\text{-butyl}$), 97 ($M^+ - 60$), 87 ($\text{NH}-(\text{CH}_3)-\text{CO}-\text{NH}^+(\text{CH}_2)^+$), 70 ($M^+ - 87$), 60 ($\text{NH}_2-\text{CO}-\text{NH}_2^+$), 58 (base peak ($\text{NH}-\text{CO}-\text{NH}^+$)) and 57 ($\text{NH}-\text{CO}-\text{NH}_2^+$).

K-6 is a white crystalline solid with experimentally found density of 1.93 g/cm^3 . The compound prepared from different batches has been examined for its purity by TLC on silica gel plate and further confirmed by HPLC following the conditions as mentioned in the experimental section. HPLC results indicate that K-6 has the retention time 3.43 min and the estimated purity is $>95\%$.

The stability of K-6 with respect to nitrolysis and aqueous work up was confirmed by stirring the material in 2:1 (v/v) mixture of acetic anhydride and 90% fuming HNO_3 at -10°C for 5 min. The suspension was warmed to room temperature and allowed to stir for 16 h. The reaction mixture was quenched with ice and the product was collected by filtration, washed with water and dried to give K-6 in $\sim 96\%$ yield with purity $>95\%$. It appears that K-6 is more resistant to hydrolytic destruction and exhibited better hydrolytic stability than other similar compounds [8,12]. However, a comparison of hydrolysis in an acidic and base environment shows that Keto-RDX is less resistant to alkalis. The mass decrement of the

Table 1
Spectral data and elemental analyses results of TBT and Keto-RDX (K-6)

Technique	TBT	K-6 ^a
IR (KBr), ν (cm^{-1})	3226, 3058, 2974, 1662, 1532, 1422, 1364, 1305, 1104, 1028, 776	3056, 2992, 1766, 1606, 1460, 1310, 1282, 1214, 820, 782, 728
¹ H NMR (DMSO-d ₆ /TMS), δ (ppm)	1.25 (5.9H, <i>t</i> -butyl), 4.17–4.21 (d, 4H, 2CH ₂), 6.24 (bs, 2H, NH)	5.95 (s, 4H, CH ₂)
EIMS, 70 eV, m/z	157 (M^+), 158 ($M^+ + 1$), 142 ($M^+ - \text{CH}_3$), 139 ($M^+ - \text{H}_2\text{O}$), 113, 100 ($M^+ - t$ -butyl), 97 ($M^+ - \text{urea}$), 87, 70, 60, 58 (base peak), 57	236 (M^+), 218, 189, 222 (trinitrotriazine), 173 ($M^+ - \text{HNO}_3$), 143 ($M^+ - \text{HNO}_3 - \text{NO}$), 176 ($M - \text{urea}$), 120 (2NNO ₂), 116 ($M^+ - 120$), 98 (triazacyclohexanone), 84 (triazine)
Molecular formula (mol wt.)	C ₇ H ₁₅ N ₃ O (157)	C ₃ H ₄ N ₆ O ₇ (236)
Elemental analysis		
Calculated	C, 53.48; H, 9.62; N, 26.73	C, 15.15; H, 1.71; N, 35.62
Found	C, 53.12; H, 9.51; N, 26.17	C, 15.92; H, 1.65; N, 35.92

^a ¹³C NMR of K-6 was recorded in both deuterated acetonitrile and acetone solvents with TMS as internal standard. The chemical shift of carbonyl carbon was observed at δ 144 and that of methylene carbon at δ 63.5. HPLC results of K-6 shows the retention time 3.48 min with purity >95%.

sample in alkaline environment is 10 times greater than in an acidic environment with same exposure time and temperature [13]. This indicates that contact between K-6 and humidity should be limited, especially in high temperature.

The IR spectrum of K-6 exhibit absorption bands of triazine and other characteristics group frequencies. The band at 3056 cm^{-1} is due to $-\text{CH}$ stretching. The intense bands at 1766 , 1606 and 1285 cm^{-1} correspond to carbonyl frequency and to the ions of nitro groups. Other significant peaks were observed at 1460 , 1150 , 872 and 782 cm^{-1} (Table 1).

The ¹H NMR spectrum of the compound is consistent with the assigned structure. The sharp singlet at δ 5.95 corresponds to four methylene protons. The sharp signal at δ 63.5 of ¹³C NMR spectrum of K-6 correlates to methylene carbon and the weak chemical shift at δ 144 corresponds to carbonyl carbon. Solvent effect has also been observed in deuterated acetone and found no change of chemical shift values in the spectrum.

The electron impact mass spectrum of K-6 showed molecular ion peak at m/z 236 along with characteristics fragmentation species at m/z 189, 173 ($M - \text{HNO}_3$)⁺, 176 ($M - \text{Urea moiety}$), 143 ($M - \text{HNO}_3 - \text{NO}$)⁺, 130 (base peak), etc. The peak at m/z 222 arises due to the formation of stable species, 1,3,5-trinitro-1,3,5-triazacyclohexane. Another significant peak at m/z 120 corresponds to the loss of 2NNO₂ groups and subsequent loss of this group from the molecular ion peak resulted in the formation of fragmented ion at m/z 116. The significant peak at m/z 98 is due to the formation of stable fragment 1,3,5-triazacyclohexanone. The low intensity ion at m/z 84 arrives due to loss of triazine (C₃H₆N₃)⁺.

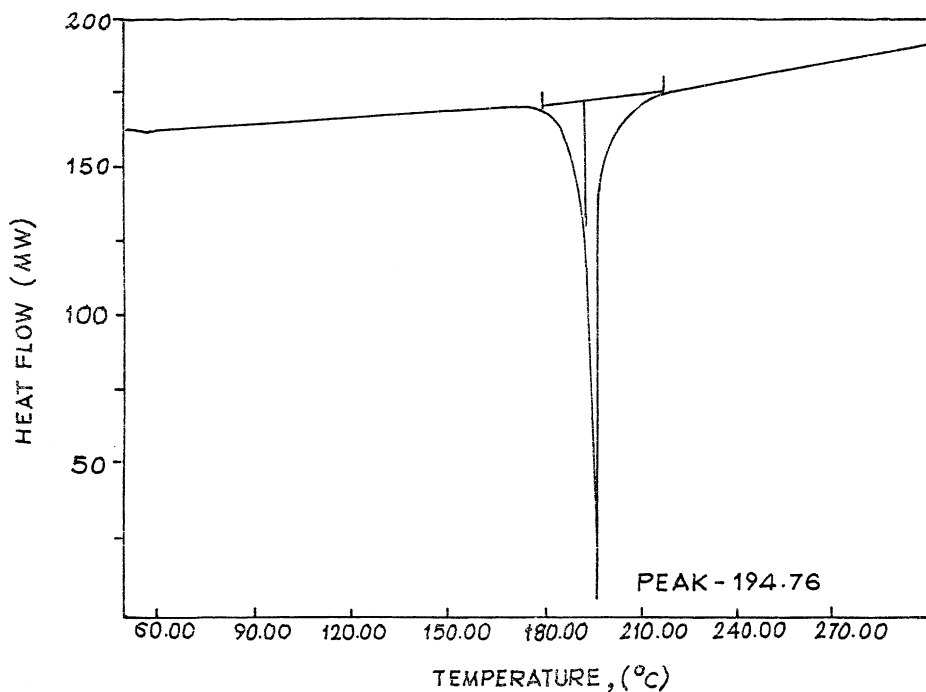


Fig. 1. DSC curve of K-6.

3.2. Thermal studies

Thermal decomposition pattern brings out that K-6 decomposes efficiently in a narrow temperature range. K-6 is expected to undergo decomposition by more or less similar mechanism like RDX. The decomposition of K-6 might be initiated by the attack of one of the NO_2 oxygen atoms on the carbonyl carbon leading to the elimination of CO_2 followed by rapid fragmentation species of CH_2O , N_2O , CO and NO . The DSC curve of K-6 (Fig. 1) at a heating rate of $10^\circ\text{C}/\text{min}$ exhibits clearly an exothermic decomposition with peak maximum at 194.76°C and energy evolved during the decomposition reaction is

Table 2

Maximum exothermic responses of K-6 as a function of scan speed

S. no.	HR ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_m (K)	$1/T_m$	$\log B$	$\ln B$	T_m^2	$\ln(\beta/T_m^2)$
1	5	193.53	466.53	2.143×10^{-3}	0.6989	1.6094	217650	-10.6812
2	10	194.76	467.76	2.1378×10^{-3}	1	2.3025	218799	-9.9933
3	15	199.386	472.386	2.1169×10^{-3}	1.1760	2.7080	223142	-9.6075
4	20	203.608	473.608	2.1114×10^{-3}	1.3010	2.9957	224296	-9.3249
5	25	203.694	476.694	2.0977×10^{-3}	1.3979	3.2188	227147	-9.1144

Activation energy (E_a), kcal/mol; source: Ozawa [14], 42; Kissinger [15], 43.

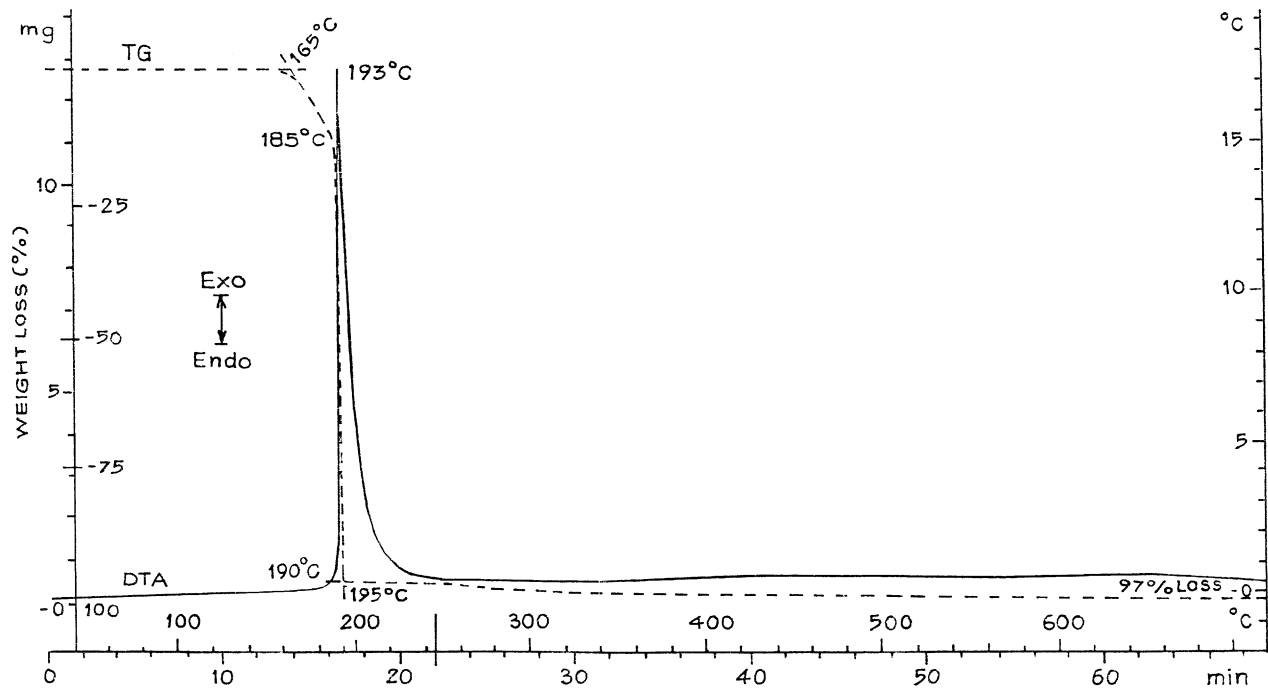


Fig. 2. Thermogram of Keto-RDX (heating rate 10°C/min, mass = 12.724 mg).

2303 J/g. Thus, K-6 has lower thermal stability. The data obtained at different heating rates are summarised in Table 2. It is seen that as the heating rate increases the temperature of exothermal peak maxima also increases. The energy of activation has been calculated by following the method of Ozawa [14] and Kissinger [15] and are found to be 42 and 43 Kcal/mol, respectively, which are in good agreement.

Fig. 2 shows the DTA and TG curve of K-6. The DTA curve shows a single sharp exotherm with peak maxima at 193 °C. The TG curve reveals characteristic, partial, two-step mass decrement before the main step of spontaneous decomposition. The weight loss starts at 165 °C and the rate of loss is slow between the temperature range from 165 to 185 °C. However, the sudden mass loss is observed immediately after 185 °C and ends at 195 °C. The total weight loss over the temperature range 165–195 °C was found to be 97%. This observation clearly indicates that the thermal decomposition of K-6 is highly exothermic in nature with almost single step decomposition reaction.

3.3. Explosive properties

K-6 has been further characterized with respect to certain explosive properties which are listed in Table 3. The sensitivity to friction and impact is determined by Julius Peter Apparatus and by the drop weight test. The data obtained indicates that K-6 is more sensitive than *N*-methyl-2,4,6-trinitrophenyl nitramine (tetryl), a well-known secondary high explosive used as booster and also as base charge in detonators and with such sensitivity K-6 can be utilized practically only in phelgmatized form. K-6 has relatively small particle size approximately 21–22 μm with typical broad distribution and often exhibited two distinct modes.

The volume of the gas released in 48 h at 94 °C is higher than that of acceptable limits. However, our separate studies (unpublished works) on the suitability of this material in propellant and explosive formulations show encouraging results. The significant reduction in sensitivity as well as increase in burn rate with lower pressure combustion limit in composite modified double base (CMDB) propellant as compared to nitramine based propellant is worth mentioning.

Table 3
Physico-chemical and explosive properties of Keto-RDX (K-6)

S. no.	Property	
1	Melting point (°C)	180–181
2	Particle size (μ)	21–22
3	Density (g/cm ³)	1.93 ± 0.05
4	DTA peak temperature (°C)	194.7
5	Deflagration temperature (°C)	181
6	Impact sensitivity, cm (height of 50% explosion, with 2 kg weight)	48
7	Friction sensitivity, kg (insensitive upto)	4
8	Velocity of detonation, m/s (calculated)	8814
9	OB (calculated; %)	–6.78
10	Detonation pressure, KBr (calculated)	379.8

4. Conclusions

Keto-RDX (K-6) has been successfully synthesized from low cost starting material and its structure is confirmed unequivocally by spectral data and elemental analysis. The compound has been evaluated for thermal and explosive properties. The exothermic decomposition of K-6 is accompanied with increase in heat release and thus establishing its potential as high energy additive. The compound has promising blend of performance and can be regarded as the most powerful energetic material among the nitro-urea explosives, synthesized so far.

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