

Studies on diaminoglyoxime (DAG): Thermolysis and evaluation as ballistic modifier in double base propellant

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Abstract

This paper reports thermolysis of diaminoglyoxime (DAG) and its evaluation as a ballistic modifier in double base propellant formulations. Differential scanning calorimetry (DSC) and simultaneous thermal analysis (DTA–thermogravimetric (TG)) revealed that DAG decomposes in two stages. Kinetics of initial stage of thermal decomposition of DAG evaluated from TG data gave activation energy (E_a) of 153 kJ mol⁻¹. The high-temperature Fourier transform Infrared (FTIR) spectra of DAG suggested preferential cleavage of N–O and C–NH₂ during decomposition. Mass spectral data also suggest possibility of similar process. The hyphenated TG–FTIR data also revealed the evolution of gases containing species, such as CN, NH, OH and oxides of nitrogen during thermal decomposition.

Evaluation of DAG as a ballistic modifier in RDX incorporated double base propellant formulations indicated that it brings down the pressure index to 0.17 compared to 0.79 for a control composition in the pressure range 6.9–8.8 MPa when used in combination with basic lead salicylate (BLS). The study suggests that combination of DAG and BLS need to be optimized to achieve more remarkable effects than BLS alone. It was observed that DAG does not have adverse effect on vulnerability and chemical stability of the propellant formulation.

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1. Introduction

Cyclic nitramines like cyclotrimethylene trinitramine (RDX) and cyclotetramethylene tetranitramine (HMX) have acquired prominence as energetic component of modern minimum signature eco-friendly propellants by virtue of their positive heat of formation (+58.5 and +75 kJ mol⁻¹, respectively), superior chemical and thermal stability as well as presence of reduced pollutants in combustion products and non-smoky exhaust similar to that of double base propellants. However, the formulations containing nitramines are beset with the major problem of high-pressure index (n) values [1,2]. According to Vieille's law, the burning rate (r) of a propellant is given by the equation, $r = aP_c^n$, wherein ' P_c ' is the chamber pressure, ' n ' the pressure index and ' a ' is a

constant. Increase in pressure index may lead to increase in burning surface there by increase in chamber pressure, which may lead to the rocket bursting of rocket.

Efforts are made to reduce the ' n ' of nitramine-based systems by conventional ballistic modifiers have met with the limited success [3–5]. A decade back, heterocyclic compound—dinitropiperazine (DNP) (ΔH_f , -54 kJ mol⁻¹), emerged as an additive capable of reducing the pressure index value of nitramine-based propellants in combination with conventional ballistic modifiers [6,7]. Compounds like diaminoglyoxime (DAG) C₂(NOH)₂(NH₂)₂ and 3,4-diaminofurazan (DAF) have elicited interest as pressure index suppressants during recent times [8,9].

Propellants having low-pressure index are generally temperature insensitive over a wide range of operating pressure and produce consistent ballistic performance. A lowering of the burning rate and pressure index value (n) in composite propellants on incorporation of DAG and DAF is reported

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by Stoner and Brill [9]. They observed that DAG and DAF thermolyse on the burning surface of the propellant to form thermally stable melamine. Fast thermolysis studies undertaken by Stoner and Brill [9] have also revealed the formation of large thermally stable cyclic azines along with the evolution of low molecular weight gases namely NH_3 , CO_2 , HCN and N_2O on decomposition of DAG and DAF. Williams et al. [8] suggested that DAG and DAF form a thermally stable cyclic azine, viz., melon (stable up to 700°C) in the superficial reaction layer of the burning surface. Such thermally stable products of decomposition are thought to retard heat transfer from the gas phase to the condensed phase.

During this work, thermal studies on DAG were undertaken by applying simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC). During STA experiments, differential thermal analysis (DTA), thermogravimetric (TG) analysis and the derivative of TG of the sample was carried out simultaneously. The residues as well as gaseous products formed on decomposition of DAG were investigated by Fourier transform Infrared (FTIR) and hyphenated TG–FTIR spectroscopy. The potential of DAG as a ballistic modifier for RDX incorporated double base propellant formulations was evaluated by determining strand-burning rates experimentally. The effect of DAG on sensitivity, compatibility and mechanical properties of propellant formulations was also investigated.

2. Experimental

2.1. Materials and methods

The starting materials used in the present study are of laboratory grade and are used directly without purification. DAG was synthesized in the laboratory on the lines of the reported procedure [10]. It was characterized by elemental analysis (Elemental Analyzer Model EA 1110, Carlo Erba Model) and FTIR spectroscopy (Perkin-Elmer, FTIR Spectrometer Model 1605). An especially designed cell, was fabricated in the lab employing a temperature programmer of Stanton Redcraft make in conjunction with a chromel–alumel thermocouple to subject the DAG sample to a high temperature. The changes in the IR pattern of DAG heated to different temperature levels were monitored [11,12].

The mass spectrum of DAG was recorded on a Finnigan make instrument (Model No. 1020); DAG (picogram quantity) filled gas capillary tube was heated electrically up to 210 – 220°C with a heating rate of $20^\circ\text{C}/\text{min}$ and the gaseous molecules of DAG were passed into continuously emitting electrons filament, wherein DAG molecules underwent excitation followed by ionization.

Thermal decomposition was studied thermogravimetrically at the heating rate of $10^\circ\text{C}/\text{min}$ by using thermal analysis system of Mettler Toledo make (TG/SDTA-8551) in nitrogen atmosphere at a purge rate of $20\text{ ml}/\text{min}$. The sample holder was made up of alumina open cup and instrument was calibrated using standard sample indium. The

Table 1

Percentage composition of various propellant ingredients in control composition (C)

Ingredients	Percentage
Nitrocellulose (NC)	49.5
Nitroglycerine (NG)	30.5
RDX	10
Diethyl phthalate (DEP)	7.0
Carbamite	3.0

temperature range employed was 30 – 600°C (with a sample mass of 3 – 4 mg). The maximum temperature attained during decomposition (T_{max}) was also recorded by TG/DTA. The gaseous decomposition products were characterized by FTIR (Bruker make, Equinox 55) in conjunction with TG. FTIR was calibrated using Polystyrene sample. Nitrogen flow at the rate of $20\text{ ml}/\text{min}$ was used to carry out evolved gases from TG furnace to FTIR detector through hot tube. FTIR detector detected the gases and the gas temperature was kept as high as possible (about 180°C) to avoid condensation of gases.

The decomposition was also followed on differential scanning calorimeter (DSC-7) of Perkin-Elmer make in nitrogen atmosphere using a sample mass of 2 mg subjected to the heating rate of $10^\circ\text{C}/\text{min}$.

Propellant formulations (Table 1) were prepared by a solvent less method and strands were extruded by standard technique [13]. Impact sensitivity was determined by a standard ‘fall hammer’ set-up, according to the ‘Bruceton staircase’ approach [14]. Friction sensitivity was assessed [15] on a Julius Peters apparatus. Stability aspects were studied based on the evolution of gaseous nitrogen oxide during heating of propellant sample by applying both qualitative (Abel’s heat test) and quantitative (Bergmann and Junk test) methods as per standard procedure [16]. The calorimetric value of propellant composition was determined in Julius Peters adiabatic bomb calorimeter. The burning rates of propellants at different pressures were determined in indigenously fabricated Crawford Bomb strand-burner equipment [17]. Mechanical properties of propellant formulations were determined on universal testing machine (Instron-1185). Flame temperature, characteristic velocity (C^*) and specific impulse of formulations were computed theoretically by using NASA CEC-71 program [18].

3. Results and discussion

3.1. Thermolysis

DSC of DAG exhibited an endotherm due to phase transition (melting) in the temperature range of 201 – 210°C followed by exothermic decomposition accompanied with release of $902\text{ J}/\text{g}$ energy in the temperature region of 209 – 253°C (Fig. 1).

The output of simultaneous TG–DTG–DTA of DAG is depicted in Fig. 2. DTG brought out that DAG undergoes two-stage decomposition in the temperature range of 170 – 228°C

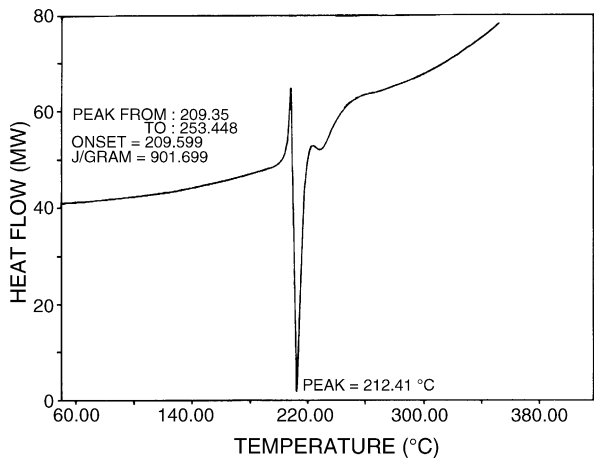


Fig. 1. DSC of DAG.

(T_{\max} 220 °C) and 228–250 °C (T_{\max} at \sim 230 °C). In TGA, the weight loss corresponding to the first and second stages of decomposition was of the order of 62 and 14%, respectively). The activation energy of 153 kJ mol⁻¹ obtained from the experimentally determined TG data by applying Coats–Redfern equation [19] is also in agreement with calculated bond dissociation energy of C–N bond [20,21].

3.2. FTIR

The room temperature and high-temperature FTIR spectrum of DAG in KBr matrix (Fig. 3) showed absorption bands corresponding to N–O bond of oxime (1446, 1298 and 942 cm⁻¹) and –NH₂ group (3368, 1674 and 794 cm⁻¹). Absorption band observed at 1574 cm⁻¹ may be attributed to the association of N–H and N–O bonds, while that at 1650 cm⁻¹ is assignable to the association of N–H (deformation) and –C=N bonds. The IR spectra of DAG, subjected to different temperatures from 170 to 480 °C

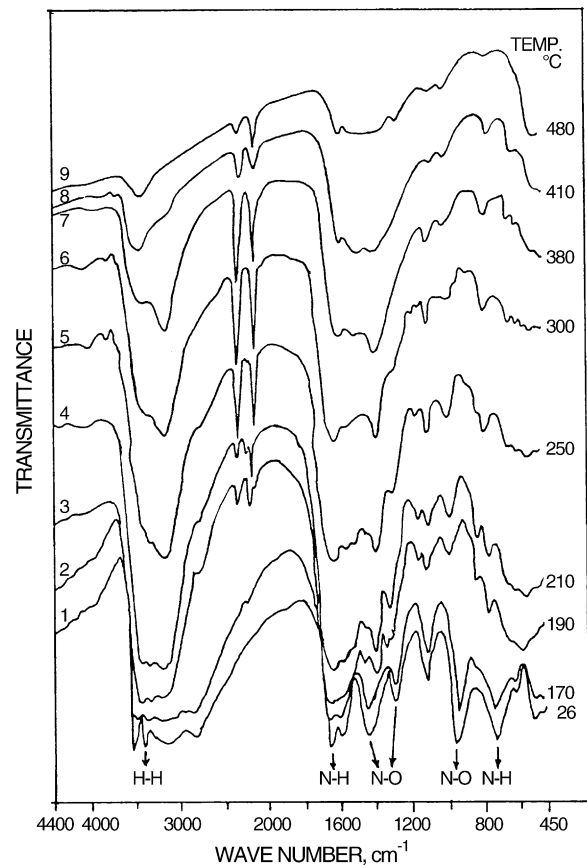


Fig. 3. High-temperature FTIR studies of DAG.

shows preferential loss in the intensity of bands assignable to N–O and –NH₂ bands. The decrease in intensity of N–O bands was relatively faster than NH₂ bands. New absorption bands appeared in the region of 2344–2170 cm⁻¹ beyond 190 °C and their intensity increased as the decomposition progressed. Absorptions at 2170 and 2224 cm⁻¹ can be

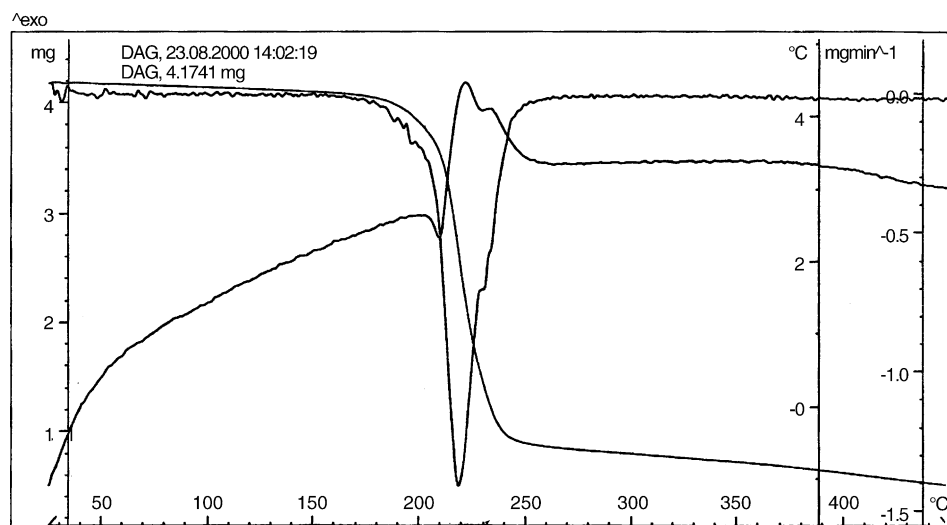


Fig. 2. TG–DTA–DTG of DAG.

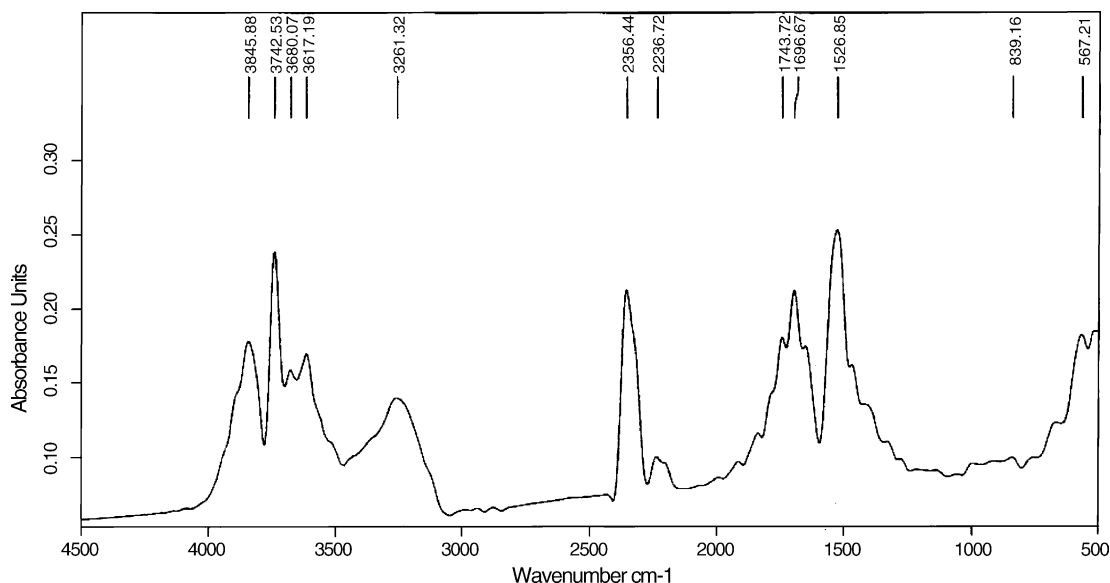


Fig. 4. TG-FTIR of evolved gases of DAG.

assigned to the presence of $\text{C}=\text{N}$ and $\text{N}^+=\text{C}=\text{N}^+$ groups. These bands reduced in intensity on increase in temperature beyond 410°C and another set of bands appeared in the region of $1615\text{--}1022\text{ cm}^{-1}$ ($\text{C}=\text{N}$ and $\text{C}-\text{N}$).

The interaction between NO and OH groups in DAG [9,22] is believed to contribute to its higher thermal stability [23,24]. However, preferential loss of IR band intensity corresponding to the $\text{N}-\text{O}$ bond suggests that cleavage of $\text{C}-\text{NO}$ is a primary step in the thermal decomposition of DAG (Fig. 3). IR spectral data of the residue suggest that the rupture of $\text{C}-\text{NO}$ bond immediately followed by the $\text{C}-\text{NH}_2$ cleavage. The deamination reaction is expected to generate NH_2 free radical in situ, which may abstract hydrogen atom to form NH_3 . The observation of additional IR bands attributed to molecular species having $\text{C}=\text{N}$, $\text{N}=\text{O}$, $\text{C}-\text{N}$ and $\text{C}=\text{O}$ bonds in conjugation, may be because of the formation of species like NH_4 [$\text{N}(\text{CN})_2$] and cyclic azines during decomposition of DAG as reported by other researchers [9].

3.3. TG-FTIR studies

The hyphenated TG-FTIR studies (Fig. 4) on DAG suggested the evolution of gaseous products containing species, such as NH (3261 cm^{-1}), OH (3845 , 3742 and 3680 cm^{-1}) and CN (2236 cm^{-1}) during thermal decomposition. The presence of IR bands at 1743 and 2356 cm^{-1} may be attributed to the evolution of gaseous species containing $\text{C}=\text{O}$ moiety. The data obtained are in agreement with the fast thermolysis studies on DAG as reported by Stoner and Brill [19].

3.4. Mass spectrum

The mass spectrum of DAG (Fig. 5) exhibited molecular ion with a mass/charge (m/z) ratio of 118, in high abundance

and its fragmentation pattern also indicates of the loss of NO (m/z 88) as well as that of OH and NH_2 subsequently (m/z at 71 and 55, respectively).

3.5. Evaluation of DAG in double base propellants

3.5.1. Thermophysical properties

Abel heat test [16] results for nitramine formulations containing DAG were found to be well within the acceptance limit of not less than 10 min for change in colour of standard

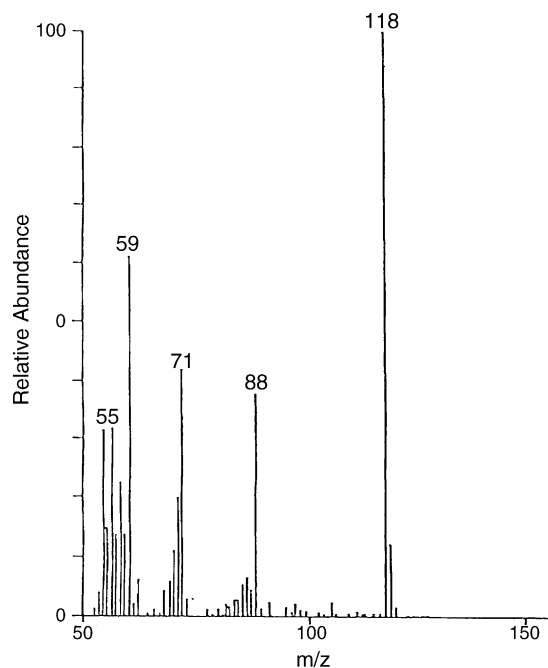


Fig. 5. Mass spectrum of DAG.

Table 2
Results of impact and friction sensitivity tests of DAG containing formulations

Propellant composition	Impact energy (J)	Impact sensitivity ($h_{50\%}$) (cm)	Friction sensitivity (kg)
Control composition (C)	0.88	44.0	24.0
C+DAG 4 parts	1.16	58.0	28.8
C+DAG 6 parts	1.20	60.0	32.4
C+BLS 2 parts+DAG 4 parts	1.28	64.0	36.0
C+BLS 2 parts+DAG 6 parts	1.48	74.0	36.0

Table 3
Mechanical properties of DAG incorporated double base propellant formulations

Properties	Control (C)	C+DAG 4 parts	C+DAG 6 parts	C+BLS 2 parts	C+BLS 2 parts+DAG 4 parts	C+BLS 2 parts+DAG 6 parts
Tensile strength (kg cm^{-2})	145	136	123	139	118	105
Elongation (%)	15	15	16	16	17	20

paper. The Bergmann and Junk (B and J) test [16] results also established compatibility of DAG with other propellant ingredients as brought out by volume of nitric oxide (NO) evolved ($2\text{--}2.4\text{ cm}^3/5\text{ g}$) on heating of sample at 120°C which was less than the upper limit of $10\text{ cm}^3/5\text{ g}$ sample.

Despite the fact that DAG is insensitive to impact and friction stimuli [14,15] the effect of its incorporation on sensitivity (Table 2) of the propellant formulations was ascertained due to its crystalline nature. The incorporation of DAG in propellant formulations led to increase in impact energy for explosion (0.88–1.48 J) and also rendered it less vulnerable to friction stimuli (insensitive up to 28–36 kg) than control (friction insensitive up to 24 kg). The low vulnerability of DAG-based formulations may be due to its negative oxygen balance (-67.74%) and lower interparticle interactions due to intramolecular hydrogen bonding. Incorporation of DAG brought down the tensile strength (TS) (Table 3). Though there is a marginal reduction in the tensile strength of DAG-based formulations in the present study, the data obtained are well within the limits of acceptable range of usable double base propellant formulation.

3.6. Burning rate

The strand-burner results obtained during this work revealed that incorporation of 2–4 parts of DAG over 100 parts composition by weight did not have any significant effect on the burning rate and pressure index of RDX incorporated propellant throughout the pressure range of 3.4–8.8 MPa. However, a combination of DAG (4 parts) with 2 parts of BLS over 100 parts of formulations resulted in burning rate enhancement to the extent of 14% (at 8.8 MPa) and brought down n -value as well. (Table 4). The mix brought down the n -value to 0.17 as against 0.79 for the control in the pressure region of 6.9–8.8 MPa. However, the burning rate and n -value realized with the composition were not remarkably different from those obtained with BLS alone.

Thus, DAG which is projected, as molecule of interest to suppress burn rate of the composite propellants, does not appear to be much effective in nitramine incorporated double base systems. It may be outcome of different chemical nature and thereby, combustion feature of the two systems. However,

Table 4
Burn rates of DAG-based formulations

Composition	Burn rate (mm/s) at pressure (MPa)				n -Value over pressure range (MPa)		
	3.4	4.9	6.8	8.8	3.4–4.9	4.9–6.8	6.8–8.8
Control (C)	4.4	5.5	6.8	8.3	0.62	0.63	0.79
C+DAG 4 parts	4.3	5.5	6.8	8.3	0.63	0.59	0.92
C+DAG 6 parts	4.3	5.2	6.6	8.1	0.53	0.7	0.82
C+BLS 2 parts	7	8.3	9.4	10	0.48	0.37	0.24
C+BLS 2 parts+DAG 4 parts	6.8	8	9.1	9.5	0.45	0.38	0.17
C+BLS 2 parts+DAG 6 parts	6.5	7.7	8.9	9.3	0.4	0.47	0.43

Table 5
Theoretical performance of DAG containing propellant formulations

Propellant composition	Flame temperature (K)	Mean molecular weight	C^* (m/s)	I_{sp} (s)
Control (C)	2308	22.52	1402	224
C+DAG 4 parts	2115	22.70	1351	216
C+DAG 6 parts	2104	22.61	1351	216

trends obtained suggest that the combination of DAG and BLS is effective.

The theoretical performance prediction of propellant formulations by NASA CEC-71 programme brought out that incorporation of DAG led to decrease in C^* (velocity of exhaust gases in the rocket motor when thrust amplification factor is one) and I_{sp} (the product of thrust and time per unit weight of the propellant) of the formulations (Table 5). The theoretically predicted characteristic velocity (C^*) and specific impulse (I_{sp}) are close to that of conventionally used double base propellant formulations.

4. Conclusion

Two-stage decomposition of DAG involving endothermic process followed by exothermic process is discernible from simultaneous thermal analysis and DSC pattern. The thermal analysis studies in conjunction with high-temperature IR suggest that initial decomposition of DAG is accompanied with the rupture of the C–NO bond. FTIR of decomposition residue as well as mass data provide complimentary evidences. DAG revealed its potential as a ballistic modifier in combination with BLS in RDX incorporated double base propellant. However, this trend is indicative and detailed investigations are necessary to understand the effect of the combination of DAG with BLS in reducing the pressure index. DAG does not adversely affect the sensitivity and stability of the propellant formulations.

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