Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 781–792

STUDIES ON AZOTETRAZOLATE BASED HIGH NITROGEN CONTENT HIGH ENERGY MATERIALS POTENTIAL ADDITIVES FOR ROCKET PROPELLANTS

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Abstract

This paper reports the synthesis, characterisation and thermolysis studies of a series of azotetrazolate salts, viz., ammonium/guanidinium/triaminoguanidinium [azotetrazolate]. TG-DTA and DSC results of these compounds exhibited their thermal stability up to 180°C. DSC indicated the highest heat release (2804 J g^{-1}) for guanidinium azotetrazolate salt during exothermic decomposition. FTIR of the decomposition products of azotetrazolate salts showed bands at 3264 and 2358 cm^{-1} which may be attributed to gaseous species such as NH_3 and HCN or NH_2CN. The sensitivity data suggests low vulnerability of ammonium and guanidinium salts. In cyclic voltammetric studies all the salts showed similar response in reduction reactions. Triamino guanidinium azotetrazolate (TAGAZ) was incorporated into solid propellant formulations in order to establish the compatibility of this class of compounds. DSC results revealed that it does not have adverse effect on thermal stability of double base matrix. The burning rate data obtained indicated that TAGAZ acts as an efficient energetic additive in composite modified double base (CMDB) propellant formulations in high-pressure region.

Keywords: ammonium azotetrazolate, azotetrazolates, guanidinium azotetrazolate, high energy materials, high nitrogen content, synthesis, TG-FTIR, thermolysis, triaminoguanidinium azotetrazolate

Introduction

Modern composite propellants derive their energy from combustion of metal fuel (Al) and components of polymeric binder (butadiene) in oxygen provided by the oxidizer generally, ammonium perchlorate (AP). High energy materials (HEMs) like, 2,4,6-trinitro toluene (TNT), trinitro triaza cyclohexane (RDX), tetranitro tetraaza cyclooctane (HMX) and hexanitro hexaaza isowurtzitane (HNIW: CL-20), despite being high explosives [1, 2] are also finding application in clean burning solid propellants. RDX and HMX derive their energy from rapid oxidation of carbon backbone by in-built oxygen as well as due to positive heat of formation. Ultra high en-

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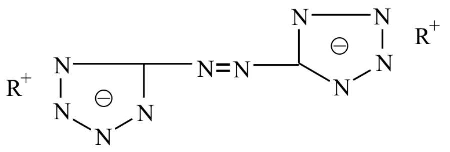
1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ergy modern compounds such as CL-20 and the recently reported hepta- and octanitrocubanes have additional feature of strained structure. The concept of new class of high nitrogen content high energy materials (HNC-HEMs) has evinced great interest [3–5] during recent time as an energetic component of propellants. Presence of N–N and C–N bonds in HNC compounds confers positive heat of formation on them. Further, HNC-HEMs produce more nitrogen gas per gram than most of the HEMs, resulting in inherently cooler combustion products, which is an attractive feature for gun propellants and gas generators. Low percentage of carbon and hydrogen in these compounds reduces the proportion of oxidized combustion products in comparison to conventional HEMs, resulting in formation of low mean molecular mass combustion products like methane [6].

Los Alamos National Laboratory (LANL), USA, reported the synthesis of three unique HNC materials based on azotetrazolate anion [7] in combination with ammonium, guanidinium and triaminoguanidinium cationic species of the following basic structure



where R$^+$ stands for (*i*) ammonium (*ii*) guanidinium and (*iii*) triaminoguanidinium.

These compounds are reported to have a combination of high positive heat of formation and insensitivity. The reported [7] heat of formation for ammonium (AAZ), guanidinium (GAZ) and triaminoguanidinium azotetrazolate (TAGAZ) salts are 98, 106 and 257 kcal mol^{-1}, respectively. Many other schools all over the globe have been actively involved in the research and development work on azotetrazolate based HEMs [8–17].

This paper reports the synthesis and characterisation of a series of azotetrazolate salts with the objective of generating additional data on this class of compounds in view of their increasing importance. Precursor (sodium azotetrazole pentahydrate) as well as products were characterised by spectroscopic methods. Thermal studies were carried out to understand decomposition pattern and the nature of gaseous decomposition products was determined by FTIR coupled with TG. The trends obtained are discussed on the lines of the reported literature. TAGAZ having the highest positive heat of formation of 257 kcal mol^{-1} in comparison to other azotetrazolates, was selected for processing of a composite modified double base (CMDB) propellant composition to establish its compatibility.

Experimental

Materials and methods

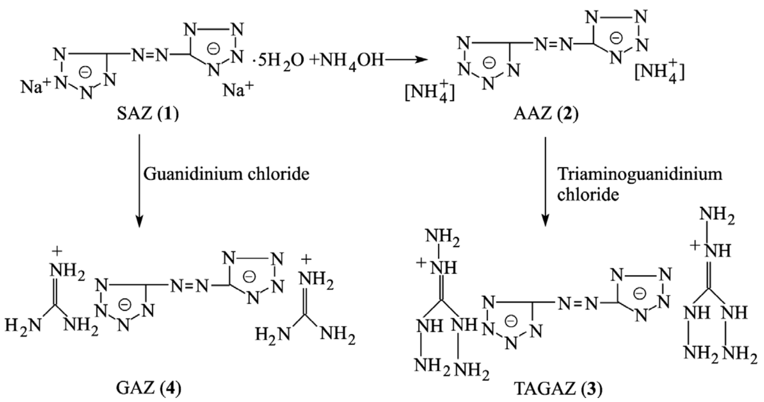
All the reagents and chemicals used in the present study were of AR grade and used as such. The IR spectra were recorded on Perkin Elmer FTIR-1600 spectrophotometer in KBr matrix. ^{1}H and ^{13}C NMR spectra were recorded on 300 MHz Varian instrument in DMSO-d_6 at 30°C with TMS as an internal standard. DSC studies were undertaken on a Perkin Elmer DSC-7 instrument operating at a heating rate of 10°C min^{-1} in a nitrogen atmosphere with 1 mg of sample. The thermal decomposition studies were also undertaken on simultaneous thermogravimetric and differential thermal analyzer (TG/SDTA) of Mettler Toledo (8551). FTIR of decomposition products was recorded on Bruker (EQUINOX-55) instrument coupled with TG. The sensitivity to impact stimuli was determined by applying standard staircase method using a 2 kg drop mass and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample [18]. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding – CE), as reference. The friction sensitivity of the compound was determined on Julius Peter's apparatus till there was no explosion/ignition in five consecutive test samples at that mass. The results obtained for impact and friction sensitivity were within the uncertainty limits of ±5 cm and ±0.2 kg, respectively. The crystal morphology was recorded on scanning electron microscope (SEM) instrument of Philips Icon make and the cyclic voltammetric studies were carried out using (CHI – 620A) electrochemical analyzer.

Burning rates were determined at laboratory scale in the pressure range of 3–9 MPa by acoustic emission technique [19]. The methodology involved the combustion of strands (6×6×100 mm) in the nitrogen pressurized steel bomb. Acoustic signals generated by the deflagrating sample were sensed by the piezoelectric transducer of resonance frequency of 200 kHz.

*Synthesis of sodium azotetrazolate pentahydrate, SAZ (**1**)*

Sodium azotetrazolate pentahydrate (SAZ, compound **1**) – a key synthon for the preparation of wide variety of energetic azotetrazolates has been synthesized and characterised following Thiele's method [7, 20].

5-Amino tetrazole monohydrate (10.3 g, 0.1 mol) was dissolved in 300 cm^{3} of 2 M sodium hydroxide solution in a stainless steel beaker of capacity of 500 cm^{3} with efficient stirring. The reaction mixture was maintained at a temperature of 60–70°C over a water bath for a period of 15 min. 12 g (0.076 mol) of powdered potassium permanganate crystals was added portion wise to the reaction mixture for a period of 1 h. The reaction mixture was stirred well and the excess permanganate was destroyed by addition of sodium sulphite solution with continuous stirring. The addition of sodium sulphite was stopped at the end point where the colour changes from green to yellow. The hot solution mixture was filtered to remove the suspended brown particles. The filtered brown solid was washed with boiling water until the washings turned to pale yellow colour. The bright yellow colour filtrate was concentrated to 300 cm^{3}



Scheme 1 Synthesis of azotetrazolates

and allowed to recrystallise in ice bath for over night. The crystals were filtered and carefully air dried to yield 21.3 g (71%) of sodium azotetrazolate penta hydrate (**1**). The synthesised SAZ was utilized for the preparation of energetic azotetrazolates viz., AAZ, TAGAZ and GAZ (Scheme 1).

Ammonium azotetrazolate (2)

Compound **1** (20 g, 0.061 mol) was dissolved in 300 cm^3 of ammonium hydroxide with stirring at 30–35°C. Ammonium chloride (25 g, 0.467 mol) was added over a period of 10 min with vigorous stirring. Ammonium azotetrazolate (**2**) began to precipitate on cooling (5°C) as a yellow solid which was filtered and air-dried to obtain 12.5 g (yield 95%) of (**2**).

Triaminoguanidinium azotetrazolate (3) and guanidinium azotetrazolate (4)

Ammonium azotetrazolate (5 g, 0.025 mol) was dissolved in 60 cm^3 of water at 80–90°C. Triaminoguanidinium chloride (7.03 g, 0.05 mol) was added to this solution under stirring and contents were allowed to cool to room temperature where upon a yellow crystalline solid formed which was filtered and air dried to yield 7.7 g (83%) of (**3**). Similarly, GAZ (**4**) was synthesised by adding guanidinium chloride to SAZ in aqueous media at 80–90°C.

The synthesised azotetrazolates were characterized by spectroscopic and thermal methods (Table 1). The synthesis of AAZ, GAZ and TAGAZ was scaled up to 50 g/batch level.

Performance evaluation

The performance evaluation of TAGAZ was carried out in CMDB propellant formulations comprising dense nitro cellulose (DNC): 30%, casting liquid (CL): 40% and TAGAZ: 30%. The components of DNC were NC (12.2% N): 90%; NG: 7%; carbamite: 3% and casting liquid consists of NG: 78%; DEP: 18% and 2-NDPA: 2%.

Table 1 Physico-chemical properties of azotetrazolates

Sr. No.	Techniques	Azotetrazolates		
		TAGAZ	AAZ	GAZ
1.	Crystal morphology – SEM	rod shaped	plate and rod shaped	rod shaped
2.	UV/nm	426 ($n\rightarrow\pi^*$), 308 ($\pi\rightarrow\pi^*$)	424 ($n\rightarrow\pi^*$), 308 ($\pi\rightarrow\pi^*$)	422 ($n\rightarrow\pi^*$), 306 ($\pi\rightarrow\pi^*$)
3.	IR/cm^{-1}	3318, 3210, 1684 (NH_2), 1450 (C=N), 1386 (C–N), 1188, 1128, 950, 774 (azotetrazolate)	3250, 3182, 1704 (NH_2), 1438 (C=N), 1390 (C–N), 1192, 1168, 1050, 776 (azotetrazolate)	3476, 3300, 1616 (NH_2), 1496 (C=N), 1398 (C–N), 1132, 1042, 978, 772 (azotetrazolate)
4.	^{1}H NMR/δ	4.46 (bs, 12H), 8.6 (s, 6H)	7.4 (bs, 4H)	7.74 (bs, 12H)
5.	^{13}C NMR/δ	158.8, 173.0	171.2	158, 173
6.	TG/°C, (mass loss%)	185–195 (24%), 200–215 (38%)	208–210 (90%)	250–255 (60%)
7.	DSC/°C, T_i	181	181	182
	T_m	204	212	259
	T_f	221	226	261
	ΔH/J g^{-1}	1352	1380	2804

The composition was prepared by adopting slurry – cast technique. The DNC was mixed with desensitised NG in a planetary mixer. AP and TAGAZ were added step by step in separate instalments to double base matrix in the mixer. Mixing was continued for 15 min without vacuum and 45 min under vacuum (10 Torr) at 25±5°C. The slurry obtained was cast under vacuum (2–5 Torr) and curing was carried out at 40±2°C for 5 days to obtain solid propellant.

Results and discussion

Spectral studies

The UV spectrum showed absorption bands in ultraviolet and visible region due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transitions (Table 1). The IR spectrum of TAGAZ showed an asymmetric $C–N_3$ ring stretching vibration at 1386 cm^{-1} and an asymmetric $C–N_2$ stretching mode of the azo group at 734 cm^{-1}. Peaks attributable to amino group appeared at 3318, 3210 and 1684, 1614 cm^{-1} corresponding to stretching and bending frequencies, respectively. In NMR spectrum, the protons of primary amino group ($–NH_2$) of triaminoguanidinium species appeared at δ 4.46, while secondary amino protons (–NH) appeared at δ 8.6.

In ^{13}C NMR of the synthesized compounds, two carbon atoms in similar environment present in azotetrazolate anion appeared at δ 171–173. The carbon atom present in guanidinium and triaminoguanidinium component of GAZ and TAGAZ appeared at δ 158.

SEM studies

The surface morphology studies of SEM showed that TAGAZ (Fig. 1) and GAZ (Fig. 2) have rod type crystal morphology while AAZ (Fig. 3) has plate type crystal morphology.

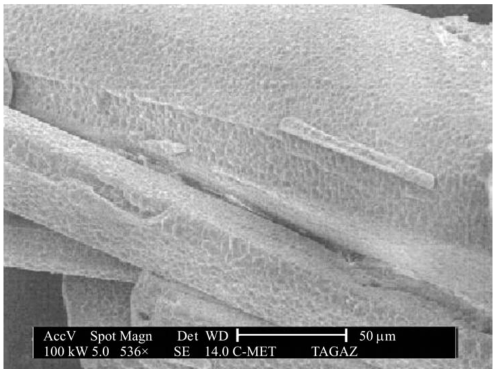


Fig. 1 SEM of TAGAZ

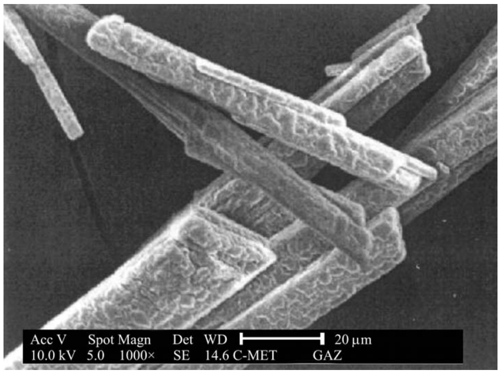


Fig. 2 SEM of GAZ

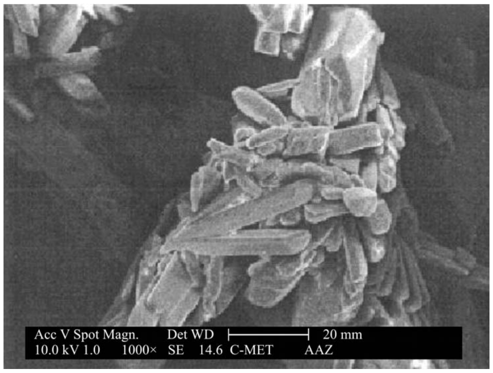


Fig. 3 SEM of AAZ

Thermal studies

DSC results revealed that the onset temperature of decomposition of AAZ, GAZ and TAGAZ is >180°C (Fig. 4). GAZ have relatively higher peak temperature (259°C) and heat release during exothermic decomposition in comparison to AAZ and TAGAZ. The TG of AAZ and GAZ (Fig. 5) showed major decomposition in the temperature range of 208–210 and 250–255°C accompanied with the mass loss of ~90 and 60%, respectively. TAGAZ revealed two major decomposition steps in the temperature range of 185–195 and 200–215°C with mass loss of 24.2 and 38.2%, respectively (Fig. 5). Relatively higher decomposition temperature of GAZ may be an outcome of strong basic nature of guanidine resulting from effective delocalisation of +ve charge in its protonated form in salt. The rupture of tetrazole ring is envisaged as a major step of decomposition of azotetrazolates studied during the investigation.

The FTIR of gaseous decomposition products during TG of TAGAZ (Fig. 6) displayed absorptions at 3258 cm^{-1} (NH) and 2357 cm^{-1} ($C\equiv N$) suggesting the presence of NH_3 and HCN or NH_2CN. Similar gaseous products obtained in AAZ and GAZ suggest that, the major decomposition process of all these compounds follows similar pattern.

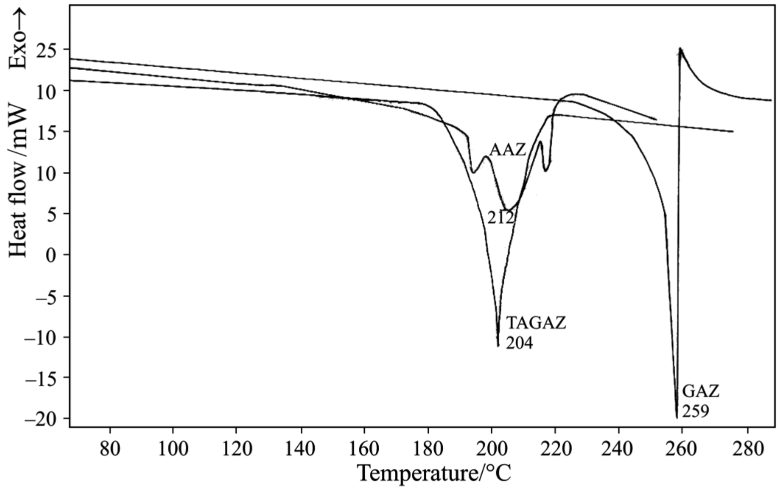


Fig. 4 DSC of AAZ, GAZ and TAGAZ

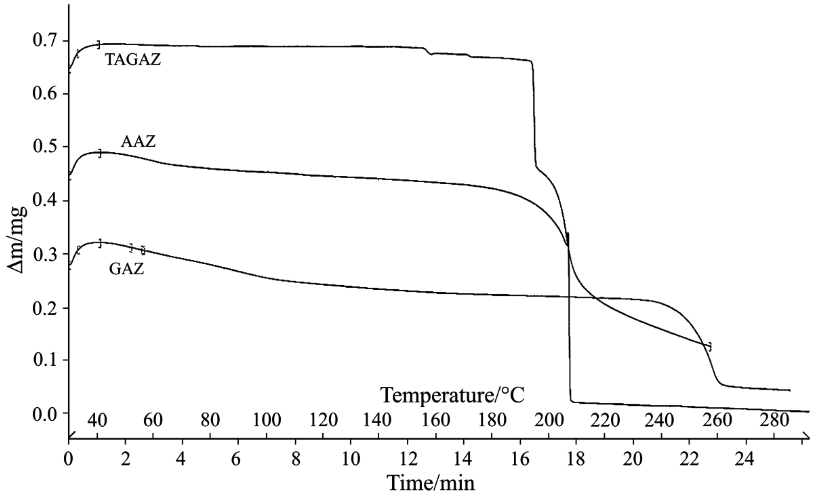


Fig. 5 TG of AAZ, GAZ and TAGAZ

Sensitivity studies

The sensitivity test results established that AAZ and GAZ are insensitive to impact and friction stimuli ($h_{50\%}$>170 cm and >36 kg) while TAGAZ exhibits relatively sensitive nature ($h_{50\%}$ 51 cm and 16 kg).

Cyclic voltammetric studies

Synthesised compounds were subjected to cyclic voltammetric studies at basic and neutral pH. The acidic pH was not selected due to reported decomposition of this

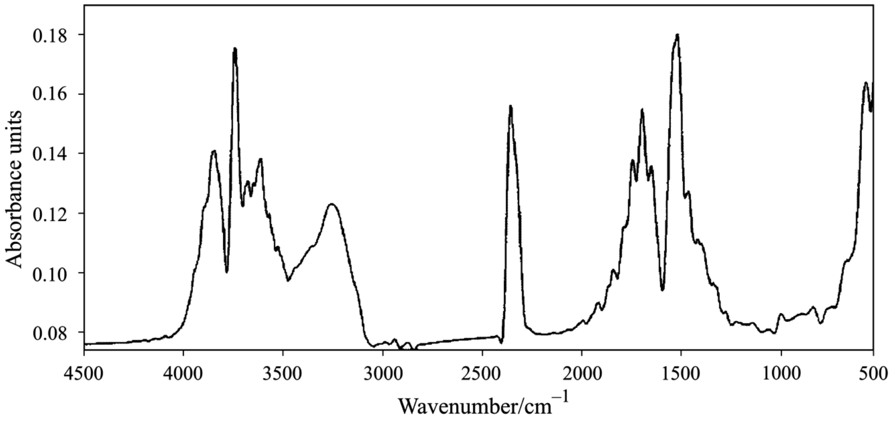


Fig. 6 TG-FTIR of TAGAZ

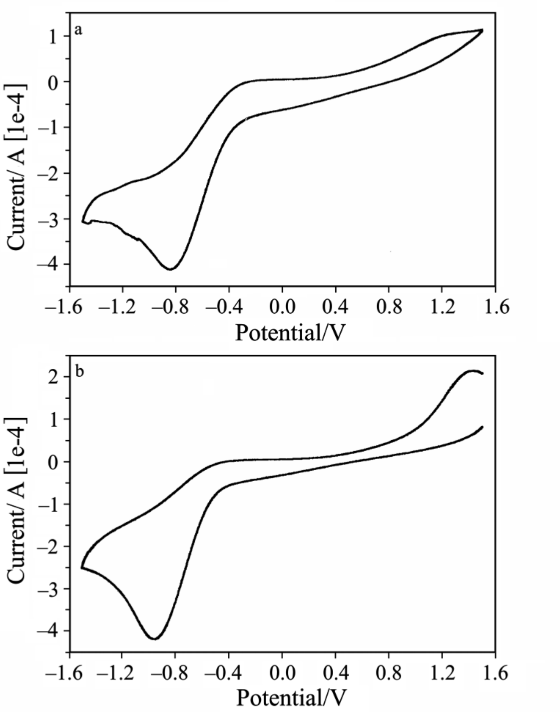


Fig. 7 Cyclic voltammetric curve of AAZ at pH a – 7 and b – 13

class of compounds in this environment [21]. Results obtained revealed that all the azotetrazolate salts are electro active in neutral and basic pH media.

The salts gave one reduction peak in both the pH media during cathodic scan in the region of –0.7 to 0.9 V potential (Figs 7–9). These features may be of interest from detection/characterization point of view of tetrazolates.

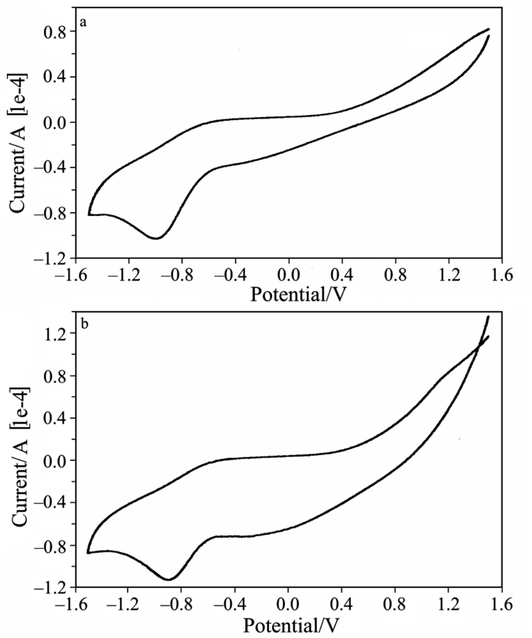


Fig. 8 Cyclic voltammetric curve of GAZ at pH a – 7 and b – 13

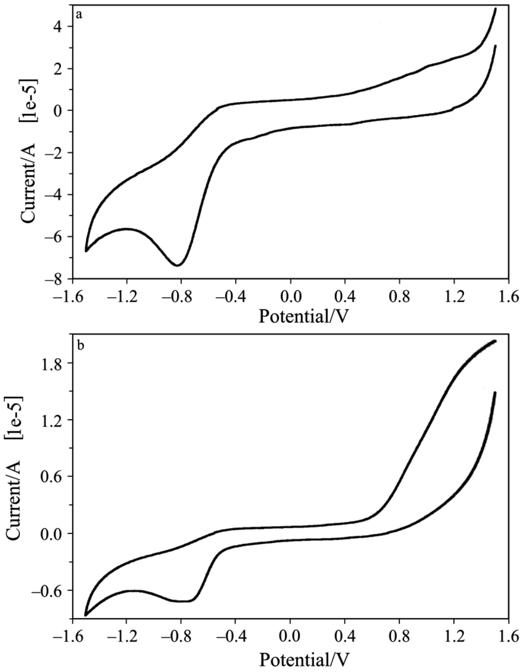


Fig. 9 Cyclic voltammetric curve of TAGAZ at pH a – 7 and b – 13

Performance evaluation

The incorporation of TAGAZ (30%) in CMDB propellant formulation gave a well-processed and cured propellant without any gasification suggesting its compatibility. This was further confirmed by DSC of TAGAZ (Fig. 10) incorporated propellant, which revealed exothermic decomposition at temperature close to that of double base matrix (187°C). The heat release during decomposition of propellant was of the order of 1468 J g^{-1}. The burning rate data obtained indicated that TAGAZ acts as an efficient energetic additive at higher pressure (>6.9 MPa) as revealed by 25% increase in burning rate (11–23 mm s^{-1}) in comparison to control formulation (11–17 mm s^{-1}) in the pressure region of 3–7 MPa.

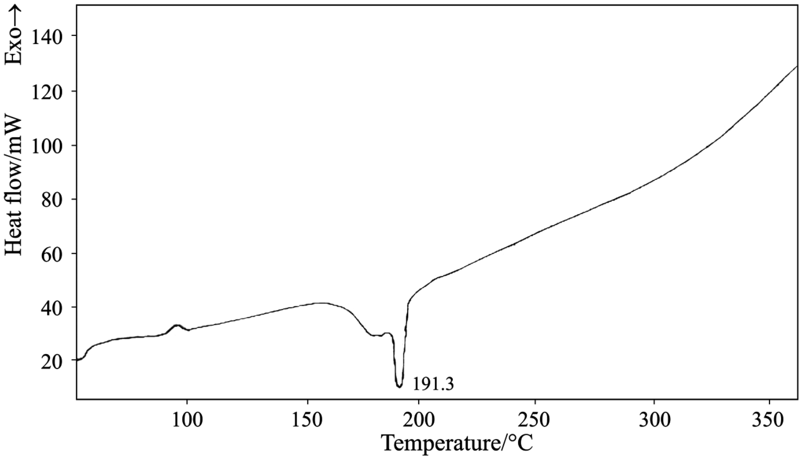


Fig. 10 DSC of TAGAZ incorporated CMDB propellant formulation

Conclusions

The synthesis and characterization of a series of azotetrazolate salts (TAGAZ, AAZ and GAZ) was established during this study. The DTA and DSC results showed that all the azotetrazolate synthesized in the present work are stable up to 180°C. TG-FTIR studies of these salts brought out that the basic decomposition mechanism remains same despite the presence of different cationic species. Impact and friction test results indicated the insensitive nature of AAZ and GAZ. Cyclic voltammetric studies suggested the electro active nature of these compounds in both neutral and basic pH media. The burning rate results obtained during this work established the potential of this class of materials in rocket propellant formulations as an energetic additive.

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The authors are grateful to Dr. Haridwar Singh, Outstanding Scientist and Director, HEMRL for constant encouragement to carry out this work. Authors also thankful to Dr. R. S. Satpute, Dr. A. N. Nazare and Dr. C. N. Divekar for their assistance in propellant processing.

References

1 M. Geetha, U. R. Nair, D. B. Sarwade, G. M. Gore, S. N. Asthana and H. Singh, J. Therm. Anal. Cal., 73 (2003) 913.

2 P. S. Makashir and E. M. Kurian, J. Therm. Anal. Cal., 55 (1999) 173.

3 D. E. Chavez, M. A. Hiskey and R. D. Gilardi, Angew. Chem., 112 (2000) 1861.

4 M. A. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout and C. A. Bolme, Progress in high nitrogen chemistry in explosives, propellants and pyrotechnics, in : Proceedings of the 27th International pyrotechnic seminar, Grand Junction, USA 2000, p. 14.

5 D. V. Chavez and M. A. Hiskey, J. Pyrotechnics, 7 (1998) 11.

6 D. E. Chavez and M. A. Hiskey, J. Energ. Mather., 17 (1999) 357.

7 M. A. Hiskey, N. Goldman and J. R. Stine, J. Energ. Mather., 16 (1998) 119.

8 J. S. Spear and P. P. Elischer, Aust. J. Chem., 35 (1982) 1.

9 G. O. Reddy and A. K. Chatterjee, Thermochim. Acta, 66 (1983) 231.

10 K. M. Bucerius, F. W. Wasmann and K. Menke, U. S. Patent No. 5,198,046, 30 March, 1993.

11 Y. L. Peng and C. W. Wong, US patent No. 5,877,300, 2 March, 1999.

12 A. Hammerl, T. M. Klapotke, H. Noth, M. Warchhold, G. Holl, M. Kaiser and U. Ticmanis, Inorg. Chem., 40 (2001) 3570.

13 V. K. Mohan and T. B. Tang, J. Chem. Phys., 79 (1983) 4271.

14 M. M. Chaudri, Mater. Sci. Lett., 3 (1984) 565.

15 D. J. Wheelan, R. J. Spear and R. W. Read, Thermochim. Acta, 80 (1984) 149.

16 A. G. Mayants, V. N. Vladimirov, N. M. Razumov and V. A. Shlyapochnikov, J. Org. Chem. USSR (Engl. Transl.) 27 (1991) 2177; Zh. Org. Khim., 11 (1991) 2450.

17 T. M. Klapotke, I. C. Tornieporth-Oetting and P. S. White, Polyhedron, 15 (1996) 2579.

18 L. Arvani and R. Hutchinson, The sensitivity of impact and friction: In energetic materials - Technology of the inorganic azide, Vol. 2, New York 1977, p. 111.

19 H. J. Rindorf, Technical review to advanced techniques in acoustical, electrical and mechanical measurements, Denmark 1981, p. 3.

20 J. Thiele, Liebigs Ann., 303 (1898) 57.

21 A. J. Berratt, L. R. Batee, J. M. Jenidne and J. R. White, U.S. Nat. Tech. Inform. Serv., AD Rep. (1971), No. 752370, Govt. Rep. Announce (U.S.), 73 (1973) 70.