

Journal of Hazardous Materials A123 (2005) 54-60

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Studies on salts of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4,6-trinitroanilino benzoic acid (TABA): Potential energetic ballistic modifiers

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Received 22 December 2004; received in revised form 6 April 2005; accepted 11 April 2005 Available online 6 June 2005

Abstract

The Co/Cu/Ni/Fe salts of 3-nitro-1,2,4-triazol-5-one (NTO) and 2,4,6-trinitroanilino benzoic acid (TABA) were prepared and characterized during this work. All the salts exhibited exothermic decomposition in DSC. The FT-IR spectra of the gaseous products evolved during TGA of NTO salts indicated the release of NO₂ and cleavage of NTO ring during the course of decomposition. Thermal decomposition of TABA salts also produced NO₂ on decomposition. The transition metal salts enhanced the burning rates of AP–HTPB composite propellant evaluated during this work. The best catalytic effect was obtained with Fe–NTO salt which increased the burning rate to the extent of ~80% as well as brought down the pressure index (*n*) to 0.18 (2–9 MPa).

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Keywords: Ballistic modifiers; Transition metals; Burning rate; Pressure index; Double base propellants; Composite propellants; NTO; TABA; Thermal decomposition

1. Introduction

Metal salts of energetic carboxylic acids belong to the category of hazardous class of explosives. Metal salts of carboxylic acids find wide application as ballistic modifiers in double base and composite modified double base (CMDB) propellants, while the transition metal oxides and ferrocenes are the preferred choice in composite propellant systems [1]. Energetic metal salts are emerging as attractive alternatives in view of their potential to ballistically modify the combustion pattern of propellants without much adverse effect on energetics. Metal salts of 3-nitro-1,2,4-triazol-5-one have been recommended as potential energetic ballistic modifiers (EBMs) for solid propellants [2]. Limited studies have been

carried out on the salts of trinitroanilino benzoic acid (TABA) in HEMRL as ballistic modifier in double base systems [3]. The acidic nature of the NTO favors the formation of a large number of salts by the deprotonation of the fourth position of the NTO ring whereas the alkali and transition metal salts of TABA result from the deprotonation of the COOH group. The metal salts of 3-nitro-1,2,4-triazol-5-one are known to decompose more readily than the corresponding parent organic moiety [4]. They are reported [2] to undergo complex decomposition processes resulting in the formation of metal oxides/carbonates/cyanates as residues. We have recently reported [5] the synthesis and performance evaluation of Li and K salts of TABA and NTO. In continuation of our work on energetic ballistic modifiers [3,5,6], this paper reports the studies on Co/Cu/Ni/Fe salts of trinitroanilino benzoic acid and 3-nitro-1,2,4-triazol-5-one to assess their potential as ballistic modifiers in ammonium perchlorate (AP)-hydroxyl terminated polybutadiene (HTPB) composite propellant. As decomposition of energetic ballistic modifiers is expected to

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^{0304-3894/\$ –} see front matter 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2005.04.010

be manifested in their catalytic effect, the compounds were subjected to thermal studies using the simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) technique. An attempt was made to characterize the decomposition products by FT-IR in conjunction with TG. The burning rates of metal salts incorporated composite propellants were determined to identify the promising candidates.

2. Experimental

2.1. Materials and methods

All the reagents of AR grade were used as such. The starting materials NTO [7] and TABA [8] were synthesized as reported in the literature. Copper nitrate, cobalt nitrate, nickel nitrate and ferric nitrate were procured from trade and used as such.

2.1.1. Synthesis

The NTO salts of transition metals $[Cu(NTO)_2(H_2O)_4, Co(NTO)_2(H_2O)_8, Ni(NTO)_2(H_2O)_8, Fe(NTO)_3]$ were prepared on the lines of reported procedures [9–12]. Corresponding TABA salts $[Cu(TABA)_2 (H_2O)_4, Co(TABA)_2(H_2O)_2, Ni(TABA)_2 (H_2O)_4$ and Fe (TABA)_3] were obtained as per the method established in HEMRL [6,8].

2.2. Characterization

The synthesized salts were characterized by IR and metal content.

Salts of 3-nitro-1,2,4-triazol-5-one: IR Spectra (KBr pellet method) $3206-3364 \text{ cm}^{-1}$ (-NH), $1620-1648 \text{ cm}^{-1}$ (C=O), 1546-1508 and $1308-1344 \text{ cm}^{-1}$ (NO₂) and $1010-1024 \text{ cm}^{-1}$ (Triazole ring).

Salts of 2,4,6-trinitroanilino benzoic acid: IR Spectra (KBr pellet method) $3328-3346 \text{ cm}^{-1}$ (-NH), $1614-1598 \text{ cm}^{-1}$ (-C=O), 1540-1542 and $1344-1348 \text{ cm}^{-1}$ (-C-NO₂), and $1408-1426 \text{ cm}^{-1}$ (C-N).

The results of elemental analysis of various salts of 3-nitro-1,2,4-triazol-5-one and 2,4,6-trinitroanilino benzoic acid are given in Table 1.

2.3. Thermal studies

Thermal decomposition pattern of the salts was studied thermo gravimetrically at the heating rate of 10°C/min, by using thermal analysis system of Mettler Toledo make (TG/SDTA-8551) in nitrogen atmosphere at a purge rate of 20 ml/min. The sample holder was made up of alumina open cup and instrument was calibrated using standard sample indium and FT-IR was calibrated using polystyrene. The temperature range employed was 30-600 °C (with a sample mass of 1-2 mg). The gaseous decomposition products were characterized by FT-IR (Bruker make - equinox 55) in conjunction with TG. Nitrogen flow at the rate of 20 ml/min was used to carry out evolved gases from TG furnace to FT-IR detector through hot tube. The gases were detected by FT-IR detector and the gas temperature was kept as high as possible (about 180 °C) to avoid condensation of gases. DSC curves were obtained by using Perkin Elmer differential scanning calorimeter (DSC-7). The sample cups were of aluminum close pan and the temperature range employed was 30-600 °C with a heating rate of 10 °C/min in nitrogen atmosphere.

2.4. Sensitivity characterization

The sensitivity of the synthesised compounds to impact stimuli was determined by applying standard Bruceton staircase method using a 2 kg drop weight and height for 50% probability of explosion ($h_{50\%}$) was determined statistically [13]. Fall Hammer apparatus was used to determine the impact sensitivity. In this test a small quantity of sample (approximately 10–20 mg) was placed on an anvil and inserted through a guide ring collar. A striker was brought to rest on top charge sandwiched between two aluminum foils (thickness 0.01 mm). A weight of known mass (2 kg) was then allowed to fall under gravitational influence, from a preselected height so as to cause the impact on striker explosive combination.

The figure of insensitivity (F of I) was computed using Tetryl (Composition Exploding – CE), as the reference. The friction sensitivity of the compound was determined on a Julius Peter's apparatus by incrementally increasing the load from 0.2-36 kg till there was no ignition/explosion in five consecutive test samples [13].

Table 1	
Results of elemental	analysis

Compound	Contents % experimental	Contents % experimentally determined (theoretical)						
	C	Н	Ν	Metal				
Cu–NTO	12.04 (12.19)	2.46 (2.5)	29.0 (28.36)	16.15 (16.20)				
Fe-NTO	15.85 (16.25)	0.88 (0.68)	37.56 (37.92)	12.37 (12.64)				
Co-NTO	10.54 (10.41)	3.74 (3.90)	24.31 (24.29)	12.65 (12.79)				
Ni-NTO	10.32 (10.41)	3.72 (3.90)	24.48 (24.29)	12.40 (12.79)				
Cu–TABA	37.20 (37.61)	2.60 (2.65)	13.48 (13.50)	7.62 (7.66)				
Fe-TABA	42.61 (42.66)	1.88 (1.91)	15.51 (15.31)	5.22 (5.10)				
Co-TABA	39.32 (39.54)	2.40 (2.28)	14.04 (14.19)	7.00 (7.47)				
Ni–TABA	38.10 (37.81)	2.50 (2.66)	13.92 (13.57)	7.00 (7.15)				

The impact and friction sensitivity tests for the benchmark explosives were also carried out under identical conditions to validate the data obtained in the present investigation.

2.5. Propellant preparation

Propellant compositions comprising 78% AP and 22% cross-linked polybutadiene binder along with two parts of 2,4,6-trinitroanilino benzoic acid/3-nitro-1,2,4-triazol-5-one salts over 100 parts of composition (by mass) were prepared using slurry-cast technique [14]. Binder components except curative [12% prepolymer-HTPB, 8% plasticizer-dioctyl adipate (DOA) along with 0.3% processing aid-lecithin and 0.5% cross-linker cum antioxidant-pyrogallol] were added to the planetary mixer and heated to 55 ± 3 °C in a water jacketed oven. The contents were mixed for 20 min and evacuated (2-5 Torr) for half an hour. AP [monomodal-9 µm] was added to the binder in three installments and mixed for half an hour. Mixing was continued for additional 1 h under vacuum (2-5 Torr). The contents were allowed to cool down to room temperature and curative-toluene diisocyanate (TDI) was added (1.2%) in 1:1(OH:NCO) stoichiometry with respect to HTPB. Final mixing was carried out for half an hour under vacuum. The slurry was cast in an evacuated mould (2-5 Torr) and cured at 70 °C for 8 days. Hydroxy terminated polybutadiene (molecular weight $\overline{M}n$ 2200, hydroxyl value 42 mg KOH/g, functionality 2, viscosity <70 Poises at 30 °C) manufactured by NOCIL, India was used for the present work.

2.6. Burn rate characterization

The burning rates of the propellant were measured in nitrogen pressurized (1.8–10.8 MPa) strand burner by sensing acoustics signals (transmitted through water) from deflagrating samples by piezoelectric transducer (resonance frequency 200 kHz) and recording the perturbance [15].

3. Results and discussion

3.1. Thermal studies

Both the 3-nitro-1,2,4-triazol-5-one and 2,4,6-trinitroanilino benzoic acid salts underwent multistage decomposition.

3.1.1. $M(NTO)(H_2O)(M=Cu, Co, Ni, Fe)$

DSC results obtained are depicted in Fig. 1 and TG results are given in Fig. 2. Co, Ni and Cu salts of NTO exhibited two-stage decomposition in DSC. In case of Co and Ni salts, the first stage of decomposition observed in the temperature range of 68-115 °C was endothermic. The exothermic decomposition was recorded in the second stage in the temperature range of 240-363 °C with peak decomposition temperature (Tmax) at 301 and 303 °C, respectively. Cu salt of



Fig. 1. DSC of salts of 3-nitro-1,2,4-triazol-5-one.

3-nitro-1,2,4-triazol-5-one exhibited endotherm in the temperature range of 117-149 °C followed by exothermic decomposition in the temperature range of 277-307 °C with the Tmax at 296 °C. The extent of weight loss observed in TG corresponding to the endothermic stage was 18% for Cu and 27% for Ni as well as Co salts owing to the loss of water molecules. The weight loss for second stage corresponding to exothermic decomposition was 40–44% for these salts. Fe salt of NTO, which is devoid of water molecule, recorded a single stage exothermic decomposition in DSC in the temperature region of 212–285 °C with a Tmax at 255 °C. TG of Fe–NTO also exhibited single stage weight loss amounting to 71% in the temperature range of 210–285 °C.

A typical FT-IR of the decomposition products of 3-nitro-1,2,4-triazol-5-one salts determined during this work are given in Fig. 3. The gaseous products exhibited strong absorption bands attributable to C=O (1652 cm⁻¹ in amide), CO₂ (2357 cm⁻¹) and C=N (2247 cm⁻¹) containing species, as well as NO₂ (1520 cm⁻¹ and 1308 cm⁻¹) whereas, the



Fig. 2. TG of Fe, Co, Ni and Cu salts of 3-nitro-1,2,4-triazol-5-one.



Fig. 3. TG-FT-IR of Fe salt of 3-nitro-1,2,4-triazol-5-one.

absorption band assignable to NTO ring (992 cm^{-1}) was absent. The appearance of such moieties in the FT-IR decomposition products of 3-nitro-1,2,4-triazol-5-one salts suggests that their decomposition follows pathway (Scheme 1) similar to that reported [5,16].

3.1.2. M (TABA)(H_2O)(M=Cu, Co, Ni and Fe)

The Co, Ni and Cu salts of 2,4,6-trinitroanilino benzoic acid studied during this work also exhibited two-stage decomposition in DSC (Fig. 4) like corresponding 3-nitro-1,2,4-triazol-5-one salts. The first endothermic stage was observed in the temperature range of 90–150 °C. The exotherm was observed with Tmax in the temperature region of 323-357 °C. The TG analysis of Co, Ni and Cu salts of 2,4,6-trinitroanilino benzoic acid (Fig. 5) showed a weight loss of 4.4, 7.5 and 8.6%, respectively, corresponding to endothermic stage in DSC, which can be attributed to the loss of water as in case of NTO salts. In TG, the weight loss observed for the second stage was 38-44% in the temperature range of 220–380 °C that corresponds to exothermic stage in DSC. TG of Fe–TABA exhibited exothermic decomposition in



Fig. 4. DSC of Fe, Co, Ni and Cu salts of 2,4,6-trinitroanilino benzoic acid.



Fig. 5. TG of Fe, Co, Ni and Cu salts of 2,4,6-trinitroanilino benzoic acid.



Scheme 1.



Fig. 6. TG-FT-IR of Fe salt of 2,4,6-trinitroanilino benzoic acid.

two steps, in the temperature range of 272-329 °C and 329-391 °C with a weight loss of 22% in each stage.

The FT-IR spectra (Fig. 6) of decomposition products of Fe salt of 2,4,6-trinitroanilino benzoic acid also exhibited absorption due to $C\equiv N$ (2106 and 587 cm⁻¹) containing species and NO₂ (1521 cm⁻¹). In addition, IR bands corresponding to NH (3264 cm⁻¹) containing species and CO₂ (2357 cm⁻¹) were also observed. These trends suggest that 2,4,6-trinitroanilino benzoic acid salts also release NO₂ on decomposition like 3-nitro-1,2,4-triazol-5-one salts. Formation of CO₂ might have occurred due to decomposition of COO⁻ group. The NH and C \equiv N containing species might have formed during secondary reactions. Similar decomposition products were observed in case of Cu, Ni and Co salts of TABA.

3.2. Sensitivity studies

The metal salts synthesised are insensitive towards impact and friction stimuli ($h_{50} > 170$ cm, >36 kg). The sensitivity data obtained for the benchmark explosives, such as RDX and TNT under identical conditions is in close agreement with the reported data [17]. These materials may be classified under the hazard category of 1.1 according to UN classification of explosives. Hence, these materials need to be handled by experienced HEMs chemists/scientists/technologist during their synthesis, characterization, scale up, storage,

Table 2				
Catalytic effect on	burning r	rates of	composite	propell

transport and evaluation. The unplanned initiation of these materials and the propellant formulations based on them may cause mass explosion.

3.3. Catalytic effect on burning rates of composite propellants

The exothermic decomposition of 3-nitro-1,2,4-triazol-5one and 2,4,6-trinitroanilino benzoic acid salts as well as formation of metal at molecular level on propellant surface may contribute towards their catalytic effect. The burning rates of 3-nitro-1,2,4-triazol-5-one and 2,4,6-trinitroanilino benzoic acid salts incorporated composite propellants formulation are given in Table 2.

The Cu–TABA salt enhanced burning rates to the extent of 80–95% in the pressure range of 2–3 MPa and to the order of 67–73% in the pressure region of 5–9 MPa whereas the Co and Ni–TABA salts catalyzed the burning rates merely to the extent of 10–30%. The Fe salt gave relatively higher catalytic effect (\sim 60%) in the entire pressure range studied and burning rates obtained for the composite propellant incorporating it were of the order of 8.7–15 mm/s in the pressure range of 2–9 MPa (Fig. 7).

The catalytic effect obtained with Cu–NTO was of the order of 75–95% whereas Co and Ni–NTO salts enhanced the burning rates by 20–35% in the entire pressure region studied. The best results were obtained with Fe–NTO in terms of high burning rates and low-pressure index combination (Table 2). The standard deviation on the calculated pressure index is 0.114, which indicates the reliability of the results obtained. Similarly the standard deviation in the case of burning rates over the pressure profile from 2 to 9 MPa lies between 1.2 and 2 which is also acceptable over the pressure range studied.

In view of the superior catalytic effect of Fe salts, DSC of the Fe–(TABA/NTO) salts incorporated propellant was determined with reference to the control composition. The results are summarized in Table 3 and depicted in Fig. 8. In DSC, control propellant composition exhibited an endotherm followed by two exotherms with peak decomposition temperature (Tmax) of 345 and 397 °C. The endotherm may be attributed to the morphological transition of AP and exotherms may be correlated with the decomposition of AP as reported

Catalytic effect on burning rates of composite propellant						
Composition	Burning rate (mm/s) pressure (MPa)					n (2–9 MPa)
	2	3	5	7	9	
Control	5.3	6.2	7.1	7.9	8.9	0.33
Control + 2 parts Cu-TABA	7.6	8.9	10.7	12.4	13.9	0.39
Control + 2 parts Co-TABA	5.2	6.5	8.0	9.1	10.9	0.47
Control + 2 parts Ni-TABA	6.2	6.8	7.8	9.9	11.4	0.40
Control + 2 parts Fe–TABA	8.7	9.3	11.1	12.7	14.9	0.35
Control + 2 parts Cu-NTO	10.3	11.1	12.3	13.6	14.9	0.24
Control + 2 parts Ni–NTO	5.4	6.9	8.4	10.1	11.1	0.51
Control + 2 parts Co-NTO	7.8	8.1	8.8	9.3	10.3	0.17
Control + 2 parts Fe-NTO	10.7	11.7	12.4	13.7	15.0	0.18

Control composition: AP-78%, HTPB Binder-22%.



Fig. 7. Burning rates of 3-nitro-1,2,4-triazol-5-one and 2,4,6-trinitroanilino benzoic acid incorporated propellant formulations.

 Table 3

 The DSC results of ballistically modified AP-HTPB propellants

Composition	Peak ter	<i>H</i> (J/g)		
	Endo	I Exo	II Exo	
Control	248	345	397	-647.7
Control + Fe-TABA	245	324	352	-2368.6
Control + Fe-NTO	246	334	367	-3648.8

in the literature [18]. The incorporation of Fe–NTO led to an increase in ΔH by -3000 J/g with decrease in peak decomposition temperature by $\sim 30 \,^{\circ}$ C, whereas the inclusion of Fe–TABA led to an appreciable decrease in the peak temper-



Fig. 8. DSC of propellant formulations.

ature (by ~45 °C) and increase in ΔH (2.7 times). It may be inferred from the DSC results that the inclusion of the Fe salt of NTO/TABA catalyzes the decomposition processes occurring in condensed/near gas phase, which may be resulting in pronounced catalytic effect on the burning rates. The thermal analysis performed, in this paper increases our understanding of thermal decomposition mechanism, which may be considered as a first step towards improving safety in the synthesis and characterization of these materials.

4. Conclusion

The transition metal salts of 3-nitro-1,2,4-triazol-5-one and 2,4,6-trinitroanilino benzoic acid were synthesized and characterized during this work. Thermal decomposition of these salts is an exothermic process and is envisaged to result in the formation of active moieties leading to the possibility of catalytic effect on decomposition of AP/Al composite propellants. The best catalytic effect was observed with Fe–NTO and Fe–TABA salts in terms of the combination of high burn rates and lower n values. The lower decomposition temperature of Fe–NTO salt than TABA salt may be responsible for its overall superior ballistic modifier capability. The trends obtained during this work establish the potential of these salts as effective ballistic modifier for composite propellants.

Acknowledgements

Authors are thankful to The Director, HEMRL Pune, for his constant encouragement and motivation to carry out this work. Authors wish to thank R.S. Satpute and S.J. Pawar for recording TG-FT-IR and DSC of the samples.

References

- [1] S.M. Vuga, Propellants Explosives Pyrotech. 16 (1991) 293.
- [2] G. Singh, S.P. Felix, J. Haz. Mat. A90 (2002) 1.
- [3] S.M. Pundalik, R.S. Palaiah, J.K. Nair, T. Mukundan, S.N. Singh, H. Singh, J. Energ. Mater., 19 (2001) 339.
- [4] L. Shangwen, W. Jiangming, F. Xiayun, Z. Jihua, Energ. Mater. 1 (1993) 22.
- [5] P.B. Kulkarni, G.N. Purandare, J.K. Nair, M.B. Talawar, T. Mukundan, S.N. Asthana, Synthesis, characterization and thermolysis studies of alkali metal salts of TABA and NTO: performance evaluation in composite propellants, J. Haz. Mat. (accepted, December 2004).
- [6] J.K. Nair, M.B. Talawar, T. Mukundan, J. Energ. Mater. 19 (2001) 155.
- [7] A. Becuwe, A. Delclos, Propellants Explosives Pyrotech. 18 (1993) 1–10.
- [8] R.S. Palaiah, N.R. Bulakh, M.B. Talawar, T. Mukundan, J. Energ. Mater. 18 (2000) 207–218.
- [9] Z. Tonglai, H. Rongzu, L. Fuping, Preparations, characterization and thermal decomposition mechanisms of metal salts of 3-nitro-1,2,4-triazol-5-one, in: O. Yuxiang (Ed.), Proceedings of the 3rd Beijing International Symposium on Pyrotechnics and Explosives, China Ordnance Society, Beijing, China, 1995, pp. 303–306.
- [10] G. Singh, I.P.S. Kapoor, S.K. Tiwari, S.P. Felix, Ind. J. Eng. Mater. Sci. 7 (2000) 229.

- [11] G. Singh, I.P.S. Kapoor, S.K. Tiwari, Propellants Explosives Pyrotech. 27 (2002) 16–22.
- [12] Mathew W. Smith, Mathew D. Ciff, NTO based explosive formulations, A Technology Review DSTO-TR-0796.
- [13] I. Arvani, R. Hutchinson, The sensitivity of impact and friction in energetic materials, in: Technology of the Inorganic Azide, Plenum Press, New York, 1978, pp. 111–1589.
- [14] W.N. Christiansen, Proceedings of the 14th Joint Propulsion Conference on AIAA/SAE, Las Vegas, 1978, pp. 25–27.
- [15] L. An-Fang, A new method for measurement of burning rates of propellants and explosives—method of constant pressure in closed bomb, in: Proceedings of the 19th International Annual Conference of ICT on Combustion and Detonation Phenomenon, 1988, p. 49.
- [16] G. Singh, I.P.S. Kapoor, S.K. Tiwari, I.P. Singh, Ind. J. Chem. Technol. 7 (2000) 236.
- [17] Rudolf Meyer, Explosives (1932), 75 and 358.
- [18] K. Kishore, G. Prasad, Defence Sci. J. 29 (1979) 39.