

Studies on energetic compounds. Part- 34. Effect of some BEMN complexes on the condensed phase thermolysis of HTPB-AP composite solid propellants[†]

Gurdip Singh* and Durgesh Kumar Pandey

Department of Chemistry, D. D. U. Gorakhpur University, Gorakhpur-273 009, India

E-mail : gsingh4us@yahoo.com Fax : 91-551-2340459

Manuscript received 20 September 2002

Effect of some bis(ethylenediamine)metal nitrate (BEMN) complexes, i.e. $[M(en)_2](NO_3)_2$ (where, M = Cu, Co, Ni and Zn and en = ethylenediamine) during the condensed phase thermolysis of hydroxyl-terminated polybutadiene (HTPB) and ammonium perchlorate (AP) composite solid propellants (CSPs) has been studied using TG and DTA. The results indicate that the thermolysis of propellants is affected when these energetic complexes are used as burning rate modifiers in small percentage (2% by wt). Ignition delay (t_{id}) measurements on unmodified and modified propellants have been conducted to examine the effect of these additives during the rapid thermolysis of propellants. The response of the modified propellants to drop weight impact is determined to know the safety aspects. The effect of these additives on thermal decomposition of oxidizer (AP) is also investigated. Copper and cobalt complexes show considerable effect while nickel and zinc moderate effect on both propellants and AP decomposition.

Composite solid propellants (CSPs) are the most important chemical formulation extensively used in rocketry, which generates the driving force of the rocket. The most important characteristic of CSPs is performance as related to end-use and safety. Performance can be described by a variety of properties like thermal stability, shock and impact sensitivity, higher energetics (Isp), burning rate etc. Out of these, burning rate is an important parameter that is directly related to their performance. As CSPs have low inherent burning rate, small percentage of burning rate modifiers (additives) is required to tailor the burn rate to achieve the specific mission requirements. Transition metal oxides (TMOs) like CuO, Fe₂O₃, MnO₂, Ni₂O₃, CuO : Cr₂O₃ are well known ballistic modifiers for CSPs having ammonium perchlorate (AP) as oxidizer¹⁻⁸. However, effectiveness of these TMOs are reported to be concentration-dependent^{9,10}. The increase of their concentration in propellant formulation may reduce the total energy due to their non-energetic nature^{4,11}. In most cases, these metallic additives leave behind a solid residue that adversely affects the specific impulse¹². To obviate these problems, significant works are on to develop novel energetic ballistic modifiers that modify the burn rate and the energetics of the CSPs to meet requirement of a specific particular mission. Brill *et al.*¹³⁻¹⁵ developed several different experimental techniques for studying the condensed phase decomposition behavior of energetic materials and solid and

liquid propellant ingredients. Among all the experimental techniques employed thermoanalytical technique plays an important role in research and development of these composite energetic materials. We have already undertaken studies¹⁶⁻²⁰ on activities of various additives on condensed phase thermolysis of propellants and AP. Patil and Verneker²¹ reported the role of metal perchlorate amines on AP decomposition. Our research for novel energetic burning rate modifiers, have resulted some potential additives for HTPB-AP propellants like some hexamine metal perchlorate complexes^{22,24} and transition metal salts of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one)^{4,23}. Very recently, some BEMN complexes have also been found to be potential burning rate modifier for HTPB-AP propellants^{25,26}. Therefore, it was found appropriate to evaluate the effect of these BEMN complexes on condensed phase thermal decomposition of propellants and AP using TG and DTA. The t_{id} and impact sensitivity measurements have also been carried out to examine the response of these additives to rapid thermolysis and impact respectively.

Results and discussion

It is evident from TG data (Table 1) that there is a considerable reduction in degradation temperature of modified propellants than the unmodified one. The propellants containing Cu and Co complexes undergo

[†]Dedicated to Professor R. P. Rastogi.

Table 1. TG, DTA and impact sensitivity ($h_{50\%}$) data on HTPB-AP propellants

Additive	TG			DTA peak temp. (°C)		$h_{50\%}$ cm
	S_{dt} °C	F_{dt} °C	%Wt. loss	Endo	Exo	
Nil	257	295	19.8	230.7	280.5	110
	326	410	69.2	—	320.7	—
[Cu(en) ₂](NO ₃) ₂	246	310	90.2	228.3	250.2	108
	340	365	5.8	—	293.5	—
[Co(en) ₂](NO ₃) ₂	247	319	91.5	227.8	300.8	98
	345	375	4.2	—	—	—
[Ni(en) ₂](NO ₃) ₂	251	292	20.6	232.0	310.0	80
	305	372	69.9	—	—	—
	425	452	5.1	—	—	—
[Zn(en) ₂](NO ₃) ₂	255	294	20.0	232.0	291.2	85
	310	385	69.2	—	319.0	—
	426	455	5.8	—	—	—

decomposition in two steps while three-step decomposition was observed for propellants based on Ni and Zn complexes. Out of these three steps, the thermogram patterns of the first two stages are similar to the pattern observed for pure AP decomposition. The weight-loss of first step is comparable to the low temperature decomposition (LTD) of AP^{27,28}. This step may be consistent of first step of HTPB²⁹ decomposition also. The second step corresponds to the high temperature decomposition (HTD) of AP^{27,28}. However, in the case of Cu and Co complexes, no inflection regarding LTD and HTD of AP decomposition was observed and both the steps were found to occur in a single rapid step. These two complexes catalyze the degradation of propellant to a large extent with a high rate of decomposition. The sharp weight-loss in TG is due to the condensed phase heat release on thermolysis that ultimately led to autoignition the propellant. It is also reported^{30,31} that if the heat produced on thermal decomposition can not be dissipated as rapidly as it is liberated, the charge will self-heat to ignition. The final step of decomposition of all the propellants is due to decomposition of residual HTPB, left over after first stage of thermolysis.

The data given in Table 1 clearly indicate the multistep decomposition of the propellant. The first endothermic peak in the temperature range 228–232° is due to polymorphic transition of AP from orthorhombic to cubic form¹⁶. Two exothermic peaks corresponding to LTD and HTD of AP have also been observed in case of control as well as Cu and Zn complex based propellants. However, single

exothermic peak was observed for propellants incorporated with Co and Ni complexes. It seems that these two complexes largely influence decomposition rate of propellants and LTD is immediately followed by HTD. Thus, peak separation is completely lost.

Thus, from TG and DTA results obtained on propellants, it can be inferred that the rate of decomposition is highly accelerated by Cu and Co complexes and moderately with Ni and Zn complexes. The effect of additives is largely seen in HTD and reduction is mainly in the HTD temperature. However, catalysis is observed both in LTD and HTD by Cu and Co complexes (Table 1). Lowering of LTD peak temperature from 280.5° to 250° and that of HTD from 320.7° to 293.5° was observed by the copper complex while no peak separation (exothermic) was found with Co complex. The decrease in reaction temperature, increase in reaction rate and lowering of completion of reaction temperature are also establishing the fact of better catalysis of Cu and Co complexes. Sharp exothermic peaks were observed during the DTA analysis, which indicate the enhancement in rate of decomposition by all these additives as compared to control one.

To get insight into the mechanism of thermolysis, TG and DTA analyses were carried out on pure AP and AP + complex mixtures. It is evident from phenomenological data (Table 2) that there is a considerable decrease in HTD of AP. These BEMN complexes also cause enhancement of decomposition rate, lowering of completion of decomposition temperature (mainly that of HTD) and overlapping of LTD and HTD (by Co complex). The fact that all these BEMN complexes undergo decomposition to give

Table 2. TG and DTA data profiles on AP and AP + additives

Additive	TG			DTA peak temp. (°C)	
	S_{dt} °C	F_{dt} °C	%Wt. loss	Endo	Exo
Nil	255.5	272.9	27.5	233.0	287.5
	309.5	413.4	69.7	—	419.4
[Cu(en) ₂](NO ₃) ₂	228.0	245.6	29.8	240.0	278.0
	254.4	295.0	68.5	—	359.0
[Co(en) ₂](NO ₃) ₂	228.0	250.0	28.9	227.6	314.7
	260.0	319.7	69.1	—	—
[Ni(en) ₂](NO ₃) ₂	229.0	256.5	28.8	226.7	286.5
	275.2	358.6	69.5	—	323.5
[Zn(en) ₂](NO ₃) ₂	231.5	267.7	30.0	235.6	306.7
	295.0	385.9	68.8	—	341.8

Table 3. Ignition delay (t_{id}) and activation energy for ignition (E^*) for HTPB-AP propellants

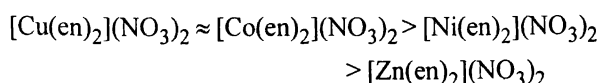
Additive	t_{id} (s) at temp. (°C)							E^* kJ mol ⁻¹
	275	300	325	350	400	425	450	
Nil	139.6 ± 0.21	113.5 ± 0.24	102.4 ± 0.17	89.7 ± 0.12	55.7 ± 0.09	36.4 ± 0.24	29.6 ± 0.23	25.7
[Cu(en) ₂](NO ₃) ₂	112.7 ± 0.20	92.7 ± 0.19	85.8 ± 0.23	62.5 ± 0.23	43.2 ± 0.06	27.8 ± 0.13	22.1 ± 0.06	23.5
[Co(en) ₂](NO ₃) ₂	113.3 ± 0.5	92.8 ± 0.08	85.0 ± 0.14	63.2 ± 0.26	44.7 ± 0.18	29.0 ± 0.21	22.9 ± 0.23	24.4
[Ni(en) ₂](NO ₃) ₂	115.6 ± 0.4	95.7 ± 0.21	87.5 ± 0.18	67.7 ± 0.19	46.7 ± 0.19	32.0 ± 0.09	24.6 ± 0.14	25.7
[Zn(en) ₂](NO ₃) ₂	119.0 ± 0.24	96.5 ± 0.15	87.6 ± 0.27	68.6 ± 0.04	46.8 ± 0.24	32.9 ± 0.23	25.0 ± 0.13	26.0

Table 4. Ignition delay (t_{id}) and activation energy for ignition (E^*) for AP and AP + additive

Additive	t_{id} (s) at temp. (°C)							E^* kJ mol ⁻¹
	400	425	450	475	500	525	550	
Nil	–	–	129.5 ± 0.27	96.6 ± 0.22	86.7 ± 0.19	54.4 ± 0.21	49.6 ± 0.13	45.5
[Cu(en) ₂](NO ₃) ₂	117.8 ± 0.10	82.4 ± 0.09	66.8 ± 0.13	42.5 ± 0.15	34.2 ± 0.16	30.8 ± 0.14	29.1 ± 0.07	24.7
[Co(en) ₂](NO ₃) ₂	115.3 ± 0.15	84.0 ± 0.18	70.0 ± 0.01	53.2 ± 0.02	41.4 ± 0.24	32.0 ± 0.01	30.4 ± 0.22	25.4
[Ni(en) ₂](NO ₃) ₂	–	105.5 ± 0.20	87.6 ± 0.24	62.4 ± 0.01	47.7 ± 0.15	37.9 ± 0.09	33.6 ± 0.24	39.6
[Zn(en) ₂](NO ₃) ₂	–	107.25 ± 0.10	89.4 ± 0.20	67.6 ± 0.14	47.8 ± 0.21	39.9 ± 0.24	34.0 ± 0.10	42.1

corresponding metal oxides as ultimate decomposition product was reported²⁵ in our earlier communication. Thus, the freshly *in situ* formed metal oxides having finer particle size and more defective sites in their crystallite would be active species in the decomposition of AP. Consequently, the rate of decomposition of propellant would be increased which in turn enhance burning rate.

Thus, from overall thermal analysis, the catalytic activities of these BEMN complexes is in the order :



The order was found²⁵ to be same for burning rate also. This indicates that activity of these additives is mainly due to condensed phase thermolysis of AP.

Ignition delay measurement is an effective technique, which is employed to understand the thermal stability of energetic materials^{4,23,25,32–34}. It is also helpful to investigate catalytic activity of various additives in CSPs^{16–18}. It is obvious from values of t_{id} (Table 3) that these additives decrease the thermal stability of propellant. Cu and Co complexes were found to be efficient in lowering of t_{id} and seem to be better additives for condensed phase reaction. However, not much difference was observed in the values of E^* . The t_{id} and E^* are in the following order : Control > Zn > Ni > Co ≈ Cu. The order of t_{id} and E^* are

same for pure AP and AP + additive mixture (Table 4).

As these complexes are of energetic nature, it was found appropriate to carryout impact sensitivity measurement to know the safety aspects pertaining to the propellants. All the BEMN complexes are inactive to impact as reported earlier²⁵. There is a marginal enhancement in sensitivity of propellants modified with Cu and Co complexes, which is evident from values of $h_{50\%}$ reported in Table 1. However, propellants based on Ni and Zn complexes, are sensitive to impact to some extent. Thus, all these complexes are potential additives for HTPB-AP propellant system, as their incorporation does not affect the sensitivity to considerable extent.

Conclusions :

All these BEMN complexes are potential energetic additives for thermolysis of propellants. Maximum and nearly equal catalytic activity and minimum impact sensitivity are of Cu and Co complexes. These two additives also catalyze the decomposition of AP to considerable extent. The catalysis may be attributed to both heat energy released during decomposition and freshly formed TMOs as decomposition product of additives. The order of activity in decomposition is same to their order of burning rate. Rapid thermolysis is also affected but not much effect is observed in impact sensitivity of propellants modified with these complexes.

Experimental

The details of material used, preparative method and measurement of burning rate of propellant were the same as reported earlier²⁵. The experimental details of thermal and impact studies are as under.

TG study : Non-isothermal TG studies on propellants (weighing ≈ 20 mg) in absence and presence of BEMN complexes as additives were undertaken in static air at a heating rate of 5° min^{-1} using home made TGA apparatus³⁵. The phenomenological data like starting decomposition temperature (S_{dt}), final decomposition temperature (F_{dt}) and weight-losses corresponding to different stages are summarized in Table 1. TG was also done on the samples of pure AP and AP containing additives (2% by wt.) in the same experimental conditions and the data are reported in Table 2.

DTA study : The derivatograms on unmodified and modified propellants (weighing ≈ 10 mg) were recorded on an Universal Thermal Analysis Instrument (Mumbai) at a constant heating rate of $10^\circ \text{ min}^{-1}$ in flowing air ($10 \text{ dm}^3/\text{h}^{-1}$) and the data are given in Table 1. Similar experiment was also performed on pure AP and AP + additive mixtures and the data profiles are presented in Table 2.

Ignition delay measurement : Ignition delay of propellant and AP (with and without additives) was determined using tube furnace (TF) technique¹⁷. The details of experimental procedure were the same as reported earlier^{17,23}. The ignition delay data were found to fit in following equation³²⁻³⁴,

$$t_{id} = A \exp E^*/RT$$

where, E^* is the activation energy for ignition and T the absolute temperature. The values of E^* were obtained from the slope of $\log t_{id}$ vs $1/T$ plot and data are presented in Tables 3 and 4 for propellant and AP, respectively.

Impact sensitivity measurement : This measurement on propellant samples was done using drop-weight impact technique in which 2 kg weight hammer was used. The description of device and experimental procedure are reported elsewhere³⁶. The data profiles are given in Table 1.

Acknowledgement

The authors are thankful to Head, Chemistry Department, DDU Gorakhpur University, Gorakhpur, for facility and DRDO, New Delhi, for financial assistance.

References

1. P. W. M. Jacob and M. R. Whitehead, *Chem. Rev.*, 1969, **69**, 551.
2. R. P. Rastogi, G. Singh and R. R. Singh, *Combust. Flame*, 1978, **33**, 305.
3. R. P. Rastogi, G. Singh and R. R. Singh, *Combust. Flame*, 1977, **30**, 117.
4. G. Singh and Prem Felix S., *Combust. Flame*, accepted.
5. H. H. Kung, "Transition Metal Oxides, Surface Chemistry and Catalysis", Elsevier, Amsterdam, 1989, Vol. 45.
6. Shin-Ming Shen, Sun-I-Chen and Bur-Horng Wu, *Thermochim. Acta*, 1993, **223**, 135.
7. R. Rajeev, K. A. Devi, A. Abraham, K. Krishnan, T. E. Krishnan, K. N. Ninan and C. G. R. Nair, *Thermochim. Acta*, 1995, **254**, 235.
8. F. Solymosi, "Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase", Wiley, New York, 1977, pp. 195-326.
9. C. H. Burnside, *AIAA*, Paper No. 75, 1975, 234.
10. R. Rajeev, C. Gopalakrishnan, K. Krishnan, K. G. Kannan and K. N. Ninan, "Third International High Energy Materials Conference and Exhibit", Thiruvananthapuram, 2000.
11. A. T. Neilson, US Pat. 3878233/1975.
12. S. R. Jain, K. C. Adiga and V. R. P. Verneker, *Combust. Flame*, 1979, **35**, 225.
13. Y. Oyumi and T. B. Brill, *Combust. Flame*, 1985, **62**, 213.
14. M. D. Timken, J. K. Chen and T. B. Brill, *Appl. Spectrosc.*, 1990, **44**, 701.
15. T. B. Brill, P. J. Brush, K. J. James, J. E. Shepherd and K. J. Pfeiffer, *Appl. Spectrosc.*, 1992, **46**, 900.
16. G. Singh and I. P. S. Kapoor, *J. Energ. Mat.*, 1993, **11**, 293.
17. G. Singh, S. K. Vasudeva and I. P. S. Kapoor, *Indian J. Technol.*, 1991, **29**, 589.
18. G. Singh, R. R. Singh, A. P. Rai and I. P. S. Kapoor, *J. Therm. Anal.*, 1990, **36**, 2539.
19. B. L. Dubey, G. Singh and C. S. Shukla, *Fuel*, 1982, **61**, 129.
20. R. P. Rastogi G. Singh and R. R. Singh, *Indian J. Chem., Sect. A*, 1977, **15**, 845.
21. K. C. Patil and V. R. P. Verneker, *Combust. Flame*, 1975, **25**, 387.
22. G. Singh and D. K. Pandey, *J. Energ. Mat.*, 2002, in press.
23. G. Singh, I. P. S. Kapoor, S. K. Tiwari, S. P. Felix, T. L. Varghese and K. N. Ninan, *J. Energ. Mat.*, 2002, accepted.
24. G. Singh and D. K. Pandey, "Thirteenth National Symposium on Thermal Analysis", Bhabha Atomic Research Centre, Mumbai, 2002, p. 86.
25. G. Singh and D. K. Pandey, *Prop. Explos. Pyro.*, 2002, accepted.
26. G. Singh and D. K. Pandey, "National Seminar on Advanced Materials", DDU Gorakhpur University, Gorakhpur, 2002, p. 99.

27. K. Kishore and K. Sridhara, "Solid Propellant Chemistry : Condensed Phase Behavior of Ammonium Perchlorate Based Solid Propellants", DESIDOC, New Delhi, 1999, p. 30.
28. S. Ramamurthy and P. G. Shrotri, *J. Energ. Mater.*, 1996, **14**, 97.
29. D. Tingfa, *Thermochim. Acta*, 1989, **138**, 189.
30. A. M. Mellor, T. L. Boggs, J. Covino, C. W. Dickinson, D. Dreftzler, L. B. Thorn, R. B. Fruy, P. W. Gibson, W. E. Roe, M. Kirshenbaum and D. M. Mann, *Prog. Energy Combust. Sci.*, 1988, **14**, 3, 213.
31. C. E. Harmance, "Solid Propellant Ignition Theories and Experiments. Fundamentals of Solid Propellant Combustion", AIAA, New York, 1984, pp. 239-304.
32. N. Semenov, "Chemical Kinetics and Chain Reactions", Clarendone Press, Oxford, 1935, Chap. 18.
33. E. S. Freeman and S. Gordon, *J. Phys. Chem.*, 1956, **60**, 867.
34. J. Zinn and R. N. Rogers, *J. Phys. Chem.*, 1962, **66**, 2646.
35. G. Singh and R. R. Singh, *Res. Ind.*, 1978, **23**, 92.
36. G. Singh, I. P. S. Kapoor, S. M. Mannan and J. P. Agarwal, *Combust. Flame*, 1994, **97**, 355.

