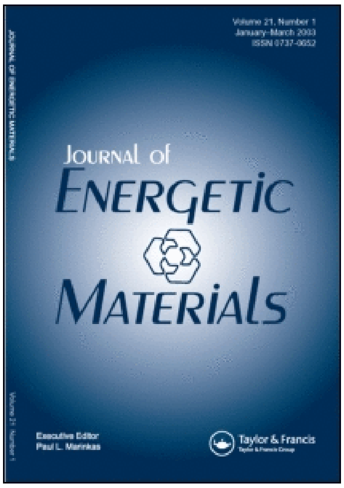


Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Explosive properties of metal salts of nitroanilinoacetic acids

K. U. B. Rao[a]; R. R. Soman[a]; Haridwar Singh[a]
[a] Explosives Research and Development Laboratory, Pune, INDIA

To cite this Article Rao, K. U. B. , Soman, R. R. and Singh, Haridwar(1990) 'Explosive properties of metal salts of nitroanilinoacetic acids', Journal of Energetic Materials, 8: 1, 99 — 109

To link to this Article: DOI: 10.1080/07370659008017248

URL: http://dx.doi.org/10.1080/07370659008017248

EXPLOSIVE PROPERTIES OF METAL SALTS OF NITROANILINOACETIC ACIDS

K.U.B.Rao, R.R.Soman and Haridwar Singh

Explosives Research and Development Laboratory,
Armament post, Pune 411 021, INDIA.

ABSTRACT

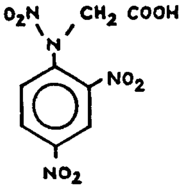
Results of impact, friction and thermal sensitivity of copper(II), silver(I) and lead(II) salts of two energetic acids, Glycine, N-(2,4 dinitro phenyl),N-nitro (1) and Glycine,N-(2,4,6 trinitro phenyl) (2) are presented. The order of thermal stability of salts of acid 1 is silver>lead>copper, while for salts of acid 2, it is copper>silver>lead. From the data generated, it is concluded that these salts can find application in propellant compositions as energetic additives.

INTRODUCTION

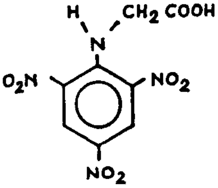
Nitroanilinoacetic acids are nitro derivatives of N-phenylglycine. Thermal decomposition characteristics of two acids 2,4,N trinitroanilino acetic acid [Glycine,N-(2,4 dinitrophenyl),N-nitro;2,4,N TNAAA;(1)]

Journal of Energetic Materials vol. 8, 099-109 (1990)
Published in 1990 by Dowden, Brodman & Devine, Inc.

and 2,4,6 trinitroanilino acetic acid [Glycine, N-(2,4,6 trinitrophenyl); 2,4,6 TNAAA;(2)], their esters [1,2] and metal salts have been investigated[3,4].



2,4,N TNAAA



2,4,6 TNAAA

Thermal decomposition studies[3,4] of metal salts indicate that they can be used in delay compositions and/or as burning rate modifiers. However, before they can be evaluated in any of these compositions, it is essential to study their stability and sensitivity characteristics which enables a research worker to take proper precautions during their processing and handling. The results of our study of some preliminary explosive properties of copper, silver and lead salts of the two acids 2,4,N TNAAA and 2,4,6 TNAAA are presented in this report.

MATERIALS AND METHODS

Acids 2,4,N TNAAA and 2,4,6 TNAAA were prepared by the methods described earlier[1,2] Copper(II), silver(I) and lead(II) salts of the two acids were prepared by adding the corresponding metal nitrate solution to a stirred aqueous solution of the sodium salt of the acid maintained at 50-60°C. The details of the methods of synthesis and characterisation have been reported separately[3,4]. All the salts were obtained as free flowing solids.

Thermal sensitivity of the metal salts was determined using a tubular furnace fabricated in the laboratory. The temperature of the furnace was monitored with a Pt vs Pt-Rh(13%) thermocouple and maintained to within ±1°C of any desired temperature using a Stanton Redcroft universal temperature programmer.The method followed was similar to that of Agrawal et al[5]. A pyrex test tube,diameter 1.4cm., thickness 0.1cm. was inserted into the furnace such that its bottom is about 0.5 cm. above the tip of the thermocouple.For each experiment, after the furnace stabilized at the desired temparature, the test tube was introduced and allowed to attain equilibrium.10 mg. of the sample was packed loosely in a thin aluminium foil and dropped into the test tube. The time interval between the time of dropping and moment of explosion was determined using a stop watch. The experiment was repeated at least three times for each temparature and the mean was taken as the explosion delay(τ)at that temparature.

The impact sensitivity of the salts was

determined using a 2 Kg. weight on an impact sensitivity apparatus fabricated in the laboratory similar to the Picatinny Arsenal impact sensitivity apparatus[6]. Friction sensitivity measurements were done on a Julius Peters friction sensitivity apparatus for high explosives.

RESULTS AND DISCUSSION

1.Thermal sensitivity:

(a) Explosion delay and activation energy:

The explosion delay (τ) at different temparatures for each of the six salts was determined as described.The relation between the explosion delay(τ) and temperature(T) can be expressed by

$$\log \tau = \log C + E/RT$$

where C is a constant,R is the universal gas constant and E is the activation energy for the process controlling the explosion delay under experimental conditions. The plots obtained for the six metal salts during the present study are shown in Fig. 1. The values of activation energy (E) calculated from the slopes are listed in table 1. This rectilinear relationship has been confirmed for a number of explosives[7].

(b) Explosion temperature and explosive phenomenon:

The explosion temperature (for a delay of 5 seconds) for each of the salts was obtained by

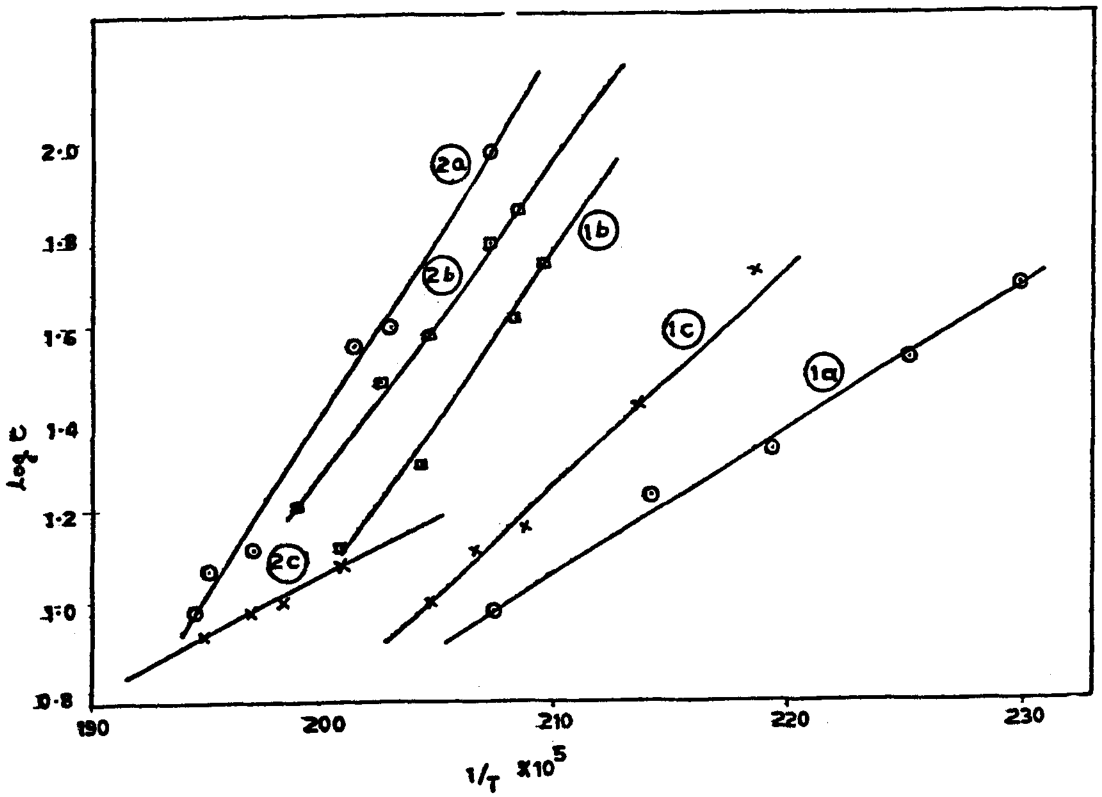


Fig.1 Variation of logτ with reciprocal of absolute temparature

TABLE 1-Thermal Properties of metal salts of Nitroanilinoacetic acids

	Metal salt	Explosion temp. (Delay 5 sec.) (°C)	Activation energy (KJ/mole)	Explosive phenomenon	Initial exo-thermic decom-position °C (Air)	Explosion delay at 200°C Sec.
1.	Copper salt of 2,4,N TNAAA(1a) $Cu[C_8H_5N_4O_8]_2.2H_2O$	237±2	54±2	Deflagarates	139.5-169.0	13.2
2.	Silver salt of 2,4,N TNAAA(1b) $Ag[C_8H_5N_4O_8]_2$	240±2	139±2	Deflagarates	180.0-201.0	76.0
3.	Lead salt of 2,4,N TNAAA(1c) $Pb[C_8H_5N_4O_8]_2$	233±2	89±2	Deflagarates with loud puff	170.0-202.5	21.4
4.	Copper salt of 2,4,6 TNAAA(2a) $Cu[C_8H_5N_4O_8]_2.2H_2O$	250±2	153±2	Deflagarates	164.0-196.5	215.0
5.	Silver salt of 2,4,6 TNAAA(2b) $Ag[C_8H_5N_4O_8]_2$	249±2	135±2	Deflagarates with loud puff	160.0-206.5	117.0
6.	Lead salt of 2,4,6 TNAAA(2c) $Pb[C_8H_5N_4O_8]_2.2H_2O$	273±2	42±2	Detonates	163.5-218.5	23.0

extrapolating the plot of log τ vs 1/T to read the temperature corresponding to τ = 5 seconds. The values are listed in table 1.

Different explosive compounds viz. initiators, high explosives, propellants are known to behave in different manner when supplied with sufficient heat stimuli. The explosive phenomenon deflagaration, detonation etc. observed for each of the six salts during the determination of explosion temperature is noted in table 1.

The explosion temperatures of the six metal salts are in the range 230-270°C and lead salt of 2,4,6 TNAAA is the only salt which detonated. The values of explosion temparature for the salts of 2,4,6 TNAAA are higher than those for corresponding salts of 2,4,N TNAAA. A comparison of these properties with those of the reported explosive properties of explosives currently in use [6,8] suggests that these salts are not powerful explosives.However, in comparison with parent acids,which undergo a very mild deflagaration and are very much less sensitive to impact , the salts appear to be better explosives.

2.Impact sensitivity:

The heights for 50% impact of the six metal salts were determined by Bruceton staircase technique [9,10]. This value and the corresponding fall energy, given by the product of impact weight(in Kg.) and the height for 50% impact (in metres) are tabulated in table 2. All the salts exploded with a loud report under test conditions.

3.Friction sensitivity:

The friction sensitivity test consists essentially of rubbing an explosive sample placed on a plane surface with another surface. A variable load is applied on moving surface to change the force of rubbing action. Each of the six metal salts gave negative results, when the test was carried out using the maximum possible load on the sliding arm corresponding to 36 Kp. The values reported[8] for some of the common high explosives Tetryl, HMX, RDX and PETN are 36, 12, 12 and 6 Kp respectively. This shows that these metal salts are insensitive to friction.

TABLE 2-Impact and Friction sensitivity of metal salts

Metal salt	Median height for 50% impact (cm.)	Fall energy (Kg.m.)	Friction sensitivity
Copper salt of 2,4,N TNAAA(1a)	74.2	1.48	No explosion upto 36 Kp.
Silver salt of 2,4,N TNAAA(1b)	83.8	1.68	No explosion upto 36 Kp.
Lead salt of 2,4,N TNAAA(1c)	97.5	1.95	No explosion upto 36 Kp.
Copper salt of 2,4,6 TNAAA(2a)	116.0	2.32	No explosion upto 36 Kp.
Silver salt of 2,4,6 TNAAA(2b)	89.0	1.78	No explosion upto 36 Kp.
Lead salt of 2,4,6 TNAAA(2c)	131.5	2.63	No explosion upto 36 Kp.

4. Thermal stability:

The time interval for which an explosive compound remains stable at a given high temperature is a measure of its thermal stability. The time for ignition delay at 200°C for each of the salts is recorded in table 1. The order of thermal stability of the salts of 2,4,N TNAAA is silver salt>lead salt>copper salt. The temperature at which initiation of thermal decomposition occurs also gives a measure of its thermal stability.This order for salts of 2,4,N TNAAA (table 1) is the same as that observed from the delay for ignition at 200°C. This is in accordance with the order of covalency of metal-ligand bonds, which are in the order Ag-O>Pb-O>Cu-O as seen from the differences in electronegativities[11]of participating atoms.

The order of thermal stability of the three salts of 2,4,6 TNAAA is copper salt>silver salt>lead salt. This order could not be counter checked from the initiation of thermal decomposition data as they decompose in a very narrow range(160-164°C). The time interval for ignition at 200°C for lead and silver salts of the two acids are in the same range. For the copper salt, however, the values are 13.2 and 215 seconds. The large value of ignition delay for copper salt of 2,4,6 TNAAA in comparison with that of 2,4,N TNAAA suggests that the former is stabilized by some unknown factors. Farmer reported that the thermal stability of a compound in solid state can be affected by hydrogen bonding, crystal lattice effect etc. in addition to molecular bonding [12].

CONCLUSIONS

Copper salt of 2,4,6 TNAAA is, thermally, the most stable of the six salts studied. The initial exothermic decomposition range of these salts is 160-200°C, which is comparable to that of NC-NG matrix. Thus, the incorporation of the salts is not likely to affect the thermal stability of double base(DB) and composite modified double base propellants(CMDB) in an adverse way. Compared to the metal salts currently in use as ballistic modifiers, whose anions do not contain any energy contributing groups, these salts are are likely to enhance the total heat output in the condensed phase during the combustion resulting in improved burning rate. They can, after checking their compatibility with the propellant components, be used as ballistic modifiers in double base type propellants.

REFERENCES

1. K.U.B. Rao and S.R. Yoganarasimhan, Proc. Ind. Acad. Sci. 95, 305 (1985).

2. K.U.B. Rao and S.R. Yoganarasimhan, Proc. Ind. Acad. Sci,95, 309 (1985).

3. K.U.B. Rao, R.R. Soman and Haridwar Singh, submitted to J. Therm. Anal.

4. K.U.B. Rao, R.R. Soman and Haridwar Singh, submitted to Thermochim. Acta.

5. S.P. Agrawal and J.P.Agrawal Ind. J. Chem.

   7,1264 (1969).

6. Encyclopedia of Explosives and Related items, B.T. Fedoroff and O.E.Sheffield Eds., Picatinny Arsenal, Dover, New Jersey, Vol. 7, I39(1975).

7. N.N. Semenov in Ref. 6, Vol. 4, D 584 (1969).

8. R. Meyer, Explosives,Verlag.Chemie.,NewYork(1977).

9. Analytical methods for Powders and Explosives. A.B. Bofors, Sweden (1974).

10. Services text book of Explosives, Ministry of Defence Publication, U.K., JSP 333 (1972).

11. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern University Edition, New Delhi, 103 (1969).

12. R.C. Farmer, J. Chem. Soc., 117, 1432 (1920).