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SYNTHESIS AND THERMAL STUDIES OF Cu(II), Ag(I) AND Pb(II) SALTS OF 2,4,6-TRINITROANILINOACETIC ACID

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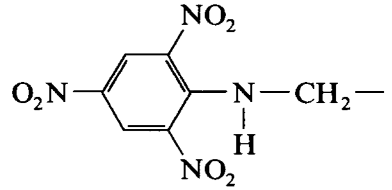
ABSTRACT

Copper(II), silver(I) and lead(II) salts of glycine-*N*-(2,4,6-trinitrophenyl) have been prepared in aqueous medium. The thermal behaviour of these salts in air and nitrogen atmospheres has been studied by thermogravimetry and differential thermal analysis. The environment has no effect on the mode of decomposition. Copper and lead salts obtained in the hydrated form, lose water followed by the organic moiety to give their respective metal oxides. Silver metal is the final residue observed during the decomposition of the silver salt. The thermal stability of the salts is in the order: copper salt > silver salt > lead salt.

INTRODUCTION

Esters and metal salts of aliphatic and aromatic acids find extensive application as plasticizers, burning-rate modifiers, etc., in propellants. The study of the thermal and explosive characteristics of potential candidates for these applications is an essential prerequisite before they can be evaluated in propellants.

Nitroanilinoacetic acids are the nitro derivatives of *N*-phenylglycine. The structure of 2,4,6-trinitroanilinoacetic acid (glycine-*N*-(2,4,6-trinitrophenyl); 2,4,6-TNAAA) is similar to that of 2,4,6-trinitrotoluene (TNT), a stable and powerful explosive. This prompted us to investigate the thermal and explosive characteristics of the acid and its metal salts. The thermal decomposition characteristics of 2,4,6-TNAAA and its methyl and ethyl esters have been reported earlier [1]. The results of our studies on the thermal behaviour of copper, silver and lead salts of 2,4,6-TNAAA are presented here. Throughout this paper, the  group is represented by R.

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EXPERIMENTAL

2,4,6-TNAAA was prepared by an intramolecular rearrangement of glycine-*N*-(2,4-dinitrophenyl)*N*-nitro in the presence of concentrated sulphuric acid as previously described [1]. To a stirred aqueous solution of the sodium salt of 2,4,6-TNAAA maintained at 50–60 ° C, was added an aqueous solution of the metal (Cu, Ag or Pb) nitrate, when the corresponding metal salt immediately precipitated. The salt was stirred for an additional 15 min. It was filtered, washed 2–3 times with water followed by ethyl alcohol and dried in air to constant weight.

Carbon, hydrogen and nitrogen contents of the complexes were determined on a Perkin–Elmer elemental analyser. The metal content was estimated by standard methods [2]. TG and DTA studies were carried out in air and nitrogen atmospheres on a Netzsch 409 thermal analyser at a heating rate of 5 ° C min^{-1}. The sample weight used was about 10 mg. Analytical grade alumina, previously dried at 700 ° C and cooled was used as the reference material.

RESULTS AND DISCUSSION

Analytical data on the three metal salts, obtained as free-flowing solids are recorded in Table 1. The data suggest that the copper and lead salts are precipitated in the hydrated form and have a metal to ligand ratio of 1 : 2. Silver salt is obtained as a 1 : 1 complex in an anhydrous form.

DTA and TG curves of the three metal salts are shown in Figs. 1–3 and the relevant data are tabulated in Table 2. A comparison of the decomposition pattern in the two atmospheres indicates that the environment around the sample has no effect on the mode of decomposition of these salts. The beginning of the decomposition of each salt and the peak temperature of the first exotherm are in the same range as that observed for the acid, whose decomposition begins at 164 ° C and finishes at 200 ° C with the peak at 189 ° C [1].

The copper salt of 2,4,6-TNAAA decomposes in two stages. In the first stage, which occurs in the temperature range 102–140 ° C, an endothermic reaction occurs. The weight loss during this stage is about 4.5% and is assigned to the dehydration process. The anhydrous salt formed, $Cu(OOCR)_2$, then decomposes with a sharp change in mass. The residue left at the end of this exothermic reaction in air and nitrogen atmospheres corresponds well with the calculated value expected for the formation of CuO from the copper salt. Comparison of its X-ray diffraction pattern with that of an authentic sample of CuO confirmed that it was CuO.

The silver salt of 2,4,6-TNAAA decomposes in a single stage in the temperature range 160–206 ° C with the peak temperature at 181–182 ° C.

TABLE 1

Analytical data of the metal complexes

Compound	Percent yield	Colour	C (%)		H (%)		N (%)		Metal (%)	
			Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
Copper salt of 2,4,6-TNAAA	87	Green	28.68	28.96	2.09	2.27	16.73	16.70	9.49	9.22
Silver salt of 2,4,6-TNAAA	78	White	24.43	24.50	1.27	1.29	14.25	14.13	27.46	26.68
Lead salt of 2,4,6-TNAAA	89	Yellow	25.47	25.60	1.72	1.40	13.77	14.12	25.47	26.05

TABLE 2

DTA and TG data of metal salts of 2,4,6-TNAAA

Compound	Atmosphere	Temp. range (° C)	Peak temp. (° C)	Type of reaction	Residue	Residue (%)	
						Found	Calculated
Copper salt of 2,4,6-TNAAA	Air	102.5–143.0	122.0	Endo.	$Cu(OOCR)_2$	95.50	94.70
		164.0–196.5	182.5	Exo.	CuO	12.50	11.87
	Nitrogen	102.5–140.5	122.0	Endo.	$Cu(OOCR)_2$	95.90	94.70
		165.0–205.0	185.5	Exo.	CuO	10.67	11.87
Silver salt of 2,4,6-TNAAA	Air	160.0–206.5	182.5	Exo.	Ag	29.61	27.46
	Nitrogen	162.5–207.0	181.0	Exo.	Ag	29.52	27.46
Lead salt of 2,4,6-TNAAA	Air	89.0–112.0	101.0	Endo.	$Pb(OOCR)_2$	96.10	95.60
		163.5–218.5	189.0	Exo.	Pb(OOCR)R	88.30	90.10
		227.5–275.0	255.5	Exo.			
		275.0–334.0	313.0	Exo.	PbO	29.58	27.45
	Nitrogen	91.0–118.0	108.0	Endo.	$Pb(OOCR)_2$	96.46	95.60
		167.0–219.0	190.0	Exo.	Pb(OOCR)R	89.00	90.10
		232.0–280.0	259.0	Exo.			
		280.0–339.0	311.0	Exo.	PbO	29.66	27.45

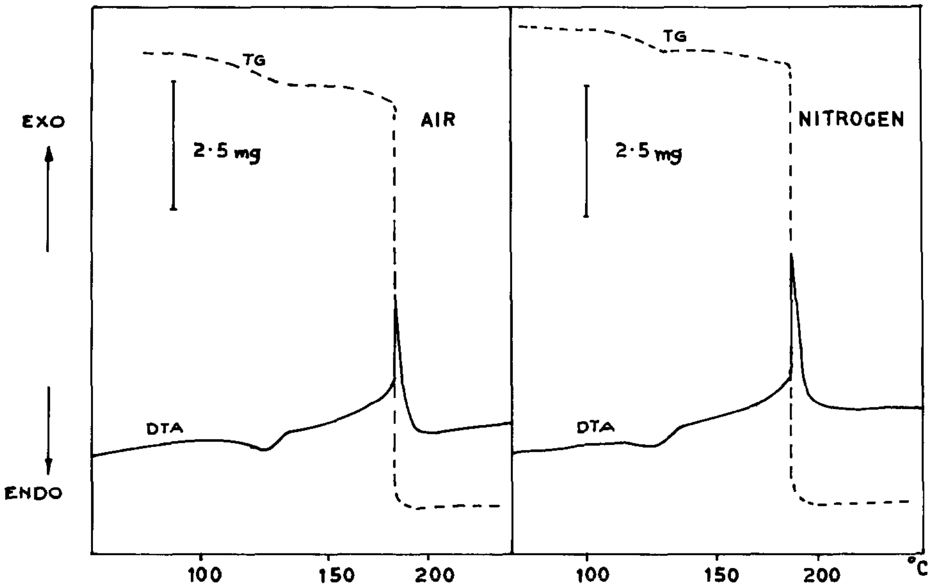

Fig. 1. Simultaneous TG and DTA curves of the copper salt of 2,4,6-TNAAA.

The residue at the end of the decomposition is 29.61 and 29.52% in air and nitrogen atmospheres respectively. Silver carboxylates are known to give silver metal as the final decomposition product [3,4]. The calculated residue for the formation of silver metal from the salt is 27.46%. Heating the residue from the silver salt in a home-made DTA instrument showed an endotherm

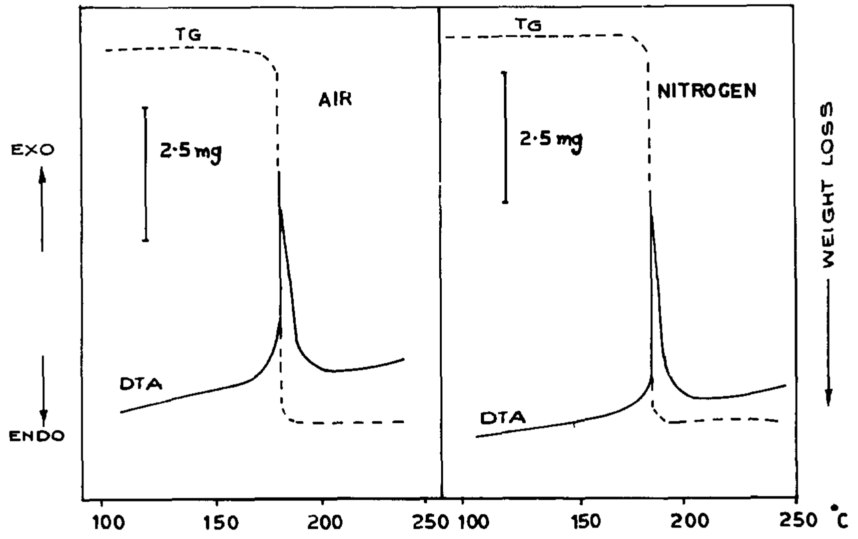

Fig. 2. Simultaneous TG and DTA curves of the silver salt of 2,4,6-TNAAA.

at 960 °C. This corresponds with the melting point of silver [5], confirming that the product is metallic silver.

The mode of decomposition of the lead salt of 2,4,6-TNAAA appears to be complex in comparison with that of the other two salts. It undergoes an endothermic reaction in the temperature range 89–120 °C accompanied by a

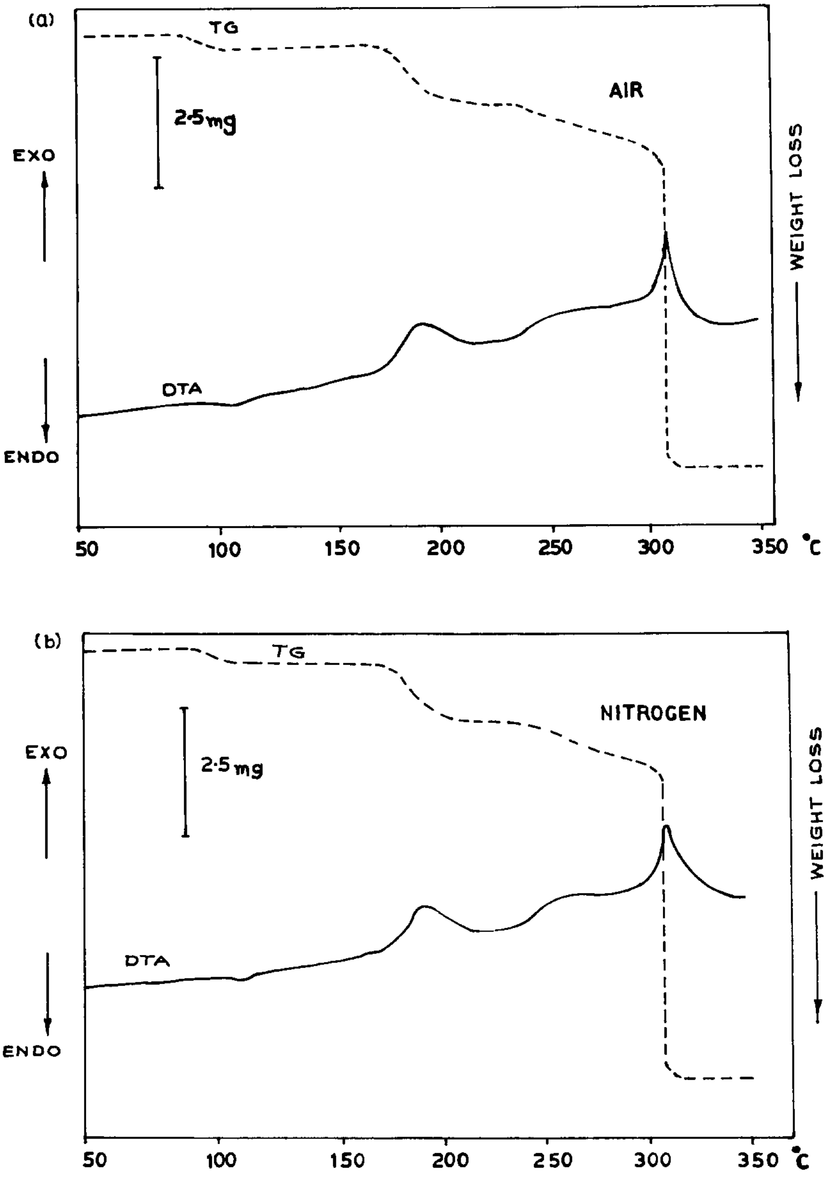

Fig. 3. Simultaneous TG and DTA curves of the lead salt of 2,4,6-TNAAA in air (a) and in nitrogen (b).

loss in weight. The weight loss is close to the value calculated for the loss of water from $Pb(OOCR)_2 \cdot 2H_2O$. Therefore, the endothermic reaction is assigned to the process of removal of two molecules of water.

The first stage of exothermic decomposition occurs with peak temperatures at 189 and 190 °C in the two atmospheres. The normal mode of decomposition of lead carboxylates is through decarboxylation [6,7]. The percent residue left at the end of the first stage decomposition corresponds favourably with the decarboxylation process. The next two exothermic reactions observed have clear-cut DTA patterns but the weight change during the two reactions overlaps. Thus, there is a gradual weight change during the first stage which culminates in a rapid weight loss during the second stage. The final residue left at the end of these decompositions in the two atmospheres was 29.58 and 29.66%. The percent residue calculated for formation of PbO from lead salt is 27.45. Comparison of the IR spectrum of the residue with that of a pure sample of PbO confirmed it to be PbO.

THERMAL STABILITY

The temperature of initiation of the exothermic decomposition is a measure of the thermal stability of a compound. The temperatures observed for the three metal salts in the present study are in a narrow range, 160–164 °C, and hence cannot be meaningfully used for judging the order of their thermal stability. It was, therefore, determined by measuring the explosion delay at 200 °C. These values for the copper, silver and lead salts were 215, 117 and 23 seconds respectively giving the order of thermal stability of these salts as copper > silver > lead. The expected order of thermal stability for the three salts on the basis of the strength of the M–O bond is silver > lead > copper. As these salts decompose in the solid state, the unusually high thermal stability of the copper salt of 2,4,6-TNAAA is attributed to factors other than the nature of bonding such as a polymeric structure, crystal lattice effects, etc. [8].

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