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SYNTHESIS AND THERMAL STUDIES OF METAL SALTS OF 2,4, N-TRINITROANILINOACETIC ACID

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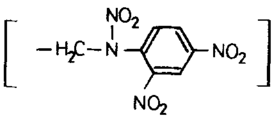
Copper(II), silver(I) and lead(II) salts of N-(2,4-dinitrophenyl)-N-nitroglycine were prepared and characterised. The thermal behaviour of the salts in air and nitrogen atmospheres was studied by means of DTA and TG techniques. The environment appeared to have no effect on the mode of decomposition. While metal oxides are formed as the end-products of decomposition of the copper and lead salts, metallic silver plus carbon was found to be final product from the silver salt. The thermal stabilities of these salts follow the sequence silver salt > lead salt > copper salt.

The present-day applications of high-energy propellants for the propulsion of rockets or missiles, and the powerful explosive compositions for warheads, demand the usage of high-energy additives to enhance the energy without affecting the processing. High-energy additives serve a number of functions, for example as energetic plasticisers, ballistic modifiers, etc.

The mode of thermal decomposition of 2,4,N-trinitroanilinoacetic acid (N-(2,4-dinitrophenyl)-N-nitroglycine; 2,4,N-TNAAA) and its esters was reported earlier [1]. Limited studies on the role of the ethyl ester of 2,4,N-TNAAA indicated its potential as an energetic plasticiser in double base (DB) propellants. The energetic nature of the acid suggested that its metal salts may be of use as energetic additives or ballistic modifiers for DB or modified double base (CMDB) propellants. However, before these salts can be evaluated for any of these applications, it is essential to study their thermal and explosive characteristics. The data thus generated enable research workers to take the required precautions during their handling. Results on the thermal behaviour of copper, silver and lead salts of 2,4,N-TNAAA are presented here. Through out this paper



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Experimental

2,4,N-TNAAA ·was prepared by the selective N-nitration of N-(2,4-dinitrophenyl)-glycine as described earlier [1]. Copper, silver and lead salts of 2,4,N-TNAAA 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°. The metal salts which precipitated immediately were digested in the mother liquor for 15 min. They were then filtered, washed 2–3 times with water followed by ethanol, and dried in air to constant weight. The carbon, hydrogen and nitrogen contents of the complexes were determined with a Perkin–Elmer elemental analyser, and the metal content of each of the salts was estimated by standard methods [2].

TG and DTA curves were recorded on a Netzsch 409 thermal analyser in air and nitrogen atmospheres at a heating rate of 5 deg/min. About 10 mg of the sample was used for each run during these thermal studies. Analytical grade alumina, previously dried at 700° for one hour and cooled, was used as the reference material.

Results and discussion

The three metal salts were obtained as crystalline free-flowing solids which were insoluble in water. The percentage yield, colour and analytical data on the three metal salts are listed in Table 1. It follows from the analytical data that the copper and lead salts were obtained with a metal to ligand ratio of 1 : 2, while the silver salt precipitated as a 1 : 1 complex. The copper salt was associated with two moles of water, while the other two salts were obtained in anhydrous form.

TG and DTA curves of the copper complex in air and nitrogen atmospheres are presented in Fig. 1, and the data for the three complexes are tabulated in Table 2. A

Table 1 Analytical data on metal salts of 2,4,N-TNAAA

Compound	Percentage yield	Colour	C, %		H, %		N, %		Metal, %	
			calc.	found	calc.	found	calc.	found	calc.	found
Cu(2,4,N-TNAAA)$_2$ $\cdot 2H_2O$	73	parrot-green	28.68	29.2	2.09	1.93	16.73	16.50	9.49	9.12
Ag(2,4,N-TNAAA)	84	white	24.43	24.87	1.27	1.43	14.25	14.20	27.46	27.13
Pb(2,4,N-TNAAA)$_2$	83	buff	24.70	24.71	1.28	1.22	14.41	14.10	26.08	26.31

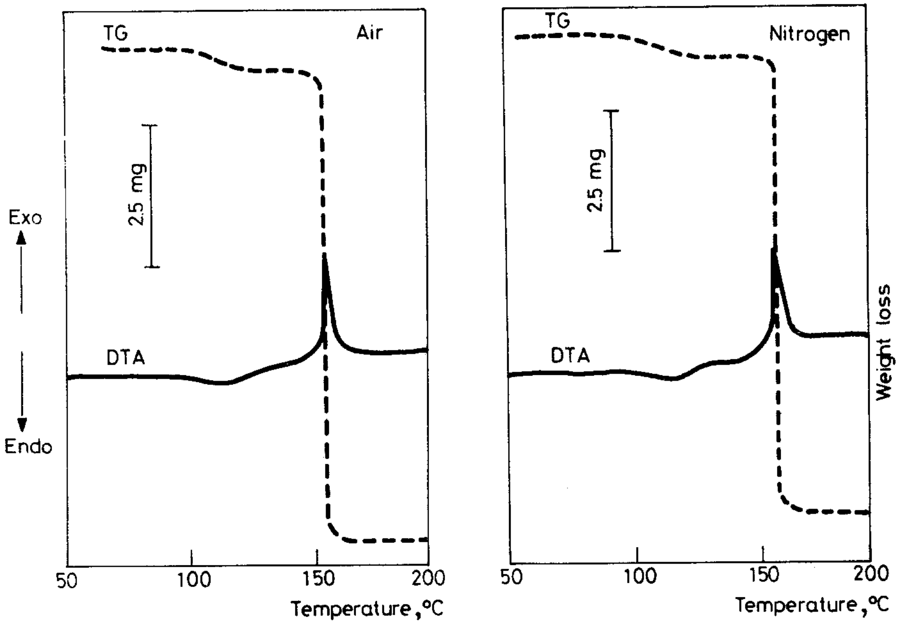

Fig. 1 TG and DTA curves for copper salt of 2,4,N-TNAAA in air and nitrogen atmospheres

comparison of the thermal curves and the data on each of the salts in air and nitrogen atmospheres suggests that the environment around the sample has little effect on the nature of the decomposition.

The copper salt, Cu(2,4,N-TNAAA)$_2 \cdot 2H_2O$, undergoes decomposition in two stages. In the first stage, which is characterised by an endothermic peak in the temperature range 90–130°, the bound water molecules are lost. The residual weight is in the range expected for the formation of the anhydrous salt. This latter undergoes a sharp exothermic decomposition in the range 140–175°, leaving a residue of 11.92% and 13% by weight in air and nitrogen atmospheres, respectively. CuO was earlier found to be the final products of decomposition of the copper complexes of N-arylgylcines [3] and dicarboxylic acids [4]. The calculated weight of the residue for the formation of CuO from the copper salt is 11.87%. The residue was identified as CuO via its X-ray diffraction pattern.

The silver salt of 2,4,N-TNAAA undergoes exothermic decomposition in two stages. In the first stage, which occurs in the temperature range 180–200°, a sharp drop in weight was observed, corresponding to a loss of about 41%. This was followed by a gradual loss in weight, which extended up to 460°. The residue left at the end of the slow decomposition was 32.85% and 39.9% in air and nitrogen atmospheres respectively.

Table 2 DTA and TG data on metal salts of 2,4,N-TNAAA

Compound	Atmosphere	Temp. range, °C	DTA peak temp., °C	Type of reaction	Residue	Percentage residue		Loss in weight, %	
						found	calc.	found	calc.
$Cu(2,4,N\text{-}TNAAA)_2 \cdot 2H_2O$	air	95.5–127	114	endothermic	$Cu(OOCR)_2$	95.71	94.70	4.29	5.3
		139.5–169	155.5	exothermic	CuO	11.92	11.87	88.08	88.13
	nitrogen	93 –129.5	115.5	endothermic	$Cu(OOCR)_2$	95.75	94.70	4.25	5.3
		149 –173.2	156.5	exothermic	CuO	13.00	11.87	87.00	88.13
Ag(2,4,N-TNAAA)	air	180 –201	185	exothermic	Ag_2R'	58.57	58.13	41.43	41.87
		201 –460	408	exothermic	Ag + C	32.85	27.46 for Ag	67.15	72.54 for Ag residue
	nitrogen	180 –200	188.5	exothermic	Ag_2R'	59.04	58.13	40.96	41.87
		201 –450	424	exothermic	Ag + C	39.9	27.46 for Ag	60.1	72.54 for Ag residue
$Pb(2,4,N\text{-}TNAAA)_2$	air	170 –202.5	182.5	exothermic	PbO	29.41	28.71	70.59	71.29
	nitrogen	165 –202	180	exothermic	PbO	28.84	28.71	71.16	71.29

Silver acetate decomposes in a single stage to give metallic silver, acetic acid and carbon dioxide as the principal products [5]. Silver arylcarboxylates are reported to decompose in two stages [6]. The residue at the end of the first stage was attributed to (Ag + C), and the final residue to metallic silver. In the present study, the residue at the end of the first stage of decomposition is about 59%. This is too large and cannot be satisfactorily assigned to (Ag + C).

The thermal decomposition characteristics of metal carboxylates are known to parallel the fragmentation pattern observed in their mass spectra [7]. The mass spectral characteristics of a number of silver carboxylates have been studied by Adams et al. [8]. Silver, the final product observed in the decomposition of silver carboxylates, contributed to the maximum intensity in their mass spectra through Ag^+ and Ag_2^+. $Ag_2R'^+$ and $Ag_2(R'COO)^+$ are among the other major ions. The intermediate formed during the decomposition of the silver salt of 2,4,N-TNAAA can correspond to either Ag_2R' or $Ag_2(R'COO)$. The calculated residual weights for the formation of Ag_2R and $Ag_2(RCOO)$ amount to 58.33% and 63.73%, respectively. As the residues left at the end of the first stage of decomposition in air and nitrogen atmospheres comprise 58.57% and 59.04%, respectively, the composition Ag_2R is assigned to this residue.

The intermediate undergoes slow decomposition to give a final product of 32.85% and 39.9% in air and nitrogen atmospheres, respectively. The calculated weight of the residue for the formation of metallic silver is 27.46%. Silver arylcarboxylates are known to give a large carbon residue together with metallic silver [6]. The additional mass observed is therefore ascribed to the carbon formed during the decomposition. In air, the oxygen available helps in the burning of part of the carbon formed. In nitrogen, the absence of this oxygen leaves a larger residue of carbon.

The lead salt of 2,4,N-TNAAA decomposed in a single stage in the temperature range 165–202°. The TG curve shows a sharp weight loss, leaving a residue of 29.41% and 28.84% in air and nitrogen atmospheres. Lead(II) carboxylates decompose to give PbO as the final product [9, 10]. The weights of the residue remaining at the end of the decomposition of the lead salt of 2,4,N-TNAAA in the two atmospheres compare well with the value expected for the formation of PbO from the salt. The residue was confirmed to be PbO from its IR spectrum. The energetics of the decomposition reaction possibly leads to the formation of PbO from the salt without the formation of any intermediate.

Conclusions

Thermal studies showed that the copper and lead salts of 2,4,N-TNAAA decompose to give the metal oxide as the final product, while metallic silver and carbon are the products of decomposition of the silver salt. The copper salt decomposes at the same temperature as the acid (151°) [1], whereas the silver and lead salts exhibit better thermal stability. In general, the temperature of initial weight loss provides an accurate estimate of the thermal stability of metal carboxylates. Thus, the sequence of thermal stability observed in the present study is Ag salt > Pb salt > Cu salt. This is in accordance with the sequence of covalency of the metal-ligand bond or the percentage ionic character of the M–O bonds, which are in the sequence Ag–O > Pb–O > Cu–O, as seen from the differences in the electronegativities of the participating atoms [11].

The results of thermal studies indicate that the salts studied in the present investigation are not likely to affect the thermal stability of DB and CMDB propellants in an adverse way. The primary exothermic decomposition temperature range of these salts coincides with that of NC and NG, the two principal constituents of propellants. Accordingly, when incorporated in propellants, they can be expected to enhance the energy output during the condensed-phase reactions of propellant burning. Both these aspects can be confirmed only by conducting actual trials with propellants.

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Zusammenfassung — Kupfer(II)-, Silber(I)- und Blei(II)-Salze von N-(2,4-Dinitrophenyl)-N-nitroglycin wurden hergestellt und charakterisiert. Mittels DTA- und TG-Techniken in Luft- und Stickstoffatmosphäre wurde das thermische Verhalten der Salze untersucht. Die Umgebung scheint auf die Art der Zersetzung keinen Einfluß zu besitzen. Zersetzungsendprodukte der Kupfer- und Bleisalze sind Metalloxide, Zersetzungsendprodukte des Silbersalzes sind elementares Silber und Kohlenstoff. Die Wärmestabilität dieser Salze sinkt in der Reihenfolge Silbersalt — Bleisalz — Kupfersalz.

Резюме — Получены и охарактеризованы соли меди, свинца и серебра с N-(2,4-динитрофенил)-N-нитроглицином. Термическое поведение солей было изучено в атмосфере воздуха и азота с помощью ДТА и ТГ. Установлено, что окружающая атмосфера не оказывает влияния на характер разложения. Конечными продуктами разложения солей меди и свинца являлись оксиды металлов. При разложение соли серебра в качестве конечных продуктов разложения были обнаружены металлическое серебро и углерод. Термоустойчивость изученных солей располагается в ряду серебро > свинец > медь.