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Note

THERMAL REACTIVITY OF DIHYDRAZINIUM NITRILOTRIACETATE

JAYANT S. BUDKULEY and A.V. VERNEKAR

Department of Chemistry, Goa University, Bambolim Goa 403 005 (India)

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ABSTRACT

The reaction between nitrilotriacetic acid (NTA) and hydrazine hydrate, a strong ligand, is studied by analysing the product formed. IR absorption frequencies and the thermoanalytical properties of this new salt, dihydrazinium nitrilotriacetate, are defined. The report forms part of the investigations of the NTA–metal ion–hydrazine hydrate system.

INTRODUCTION

Although the chelate forming behaviour of nitrilotriacetic acid (NTA) with metal ions has been described [1,2], the reaction of this tribasic acid with metal ions in the presence of hydrazine has not been investigated. Hydrazine is a strong ligand [3], and it was felt that it would be interesting to study its influence on the NTA–metal ion system. As part of the initial investigation, the reaction between NTA and hydrazine hydrate was studied by identifying the nature of the reaction product. We now report the synthesis, spectral and thermal reactivity of a new salt of NTA.

EXPERIMENTAL

About 10 ml of 20% alcoholic hydrazine hydrate, $N_2H_4 \cdot H_2O$ (99.8–99.9%) was added to 0.01 mol nitrilotriacetic acid (99–100%) with constant stirring. The product formed was precipitated out by the addition of absolute alcohol and filtered. It was then washed with ether and dried over P_2O_5 in a vacuum desiccator. The composition of the compound was established by chemical analysis and characterized by IR spectral analysis. The hydrazine content was determined by titrating against 0.025 M KIO_3 solution under Andrews [4] conditions. Estimation of *c* was carried out using a Perkin–Elmer 240 B elemental analyser.

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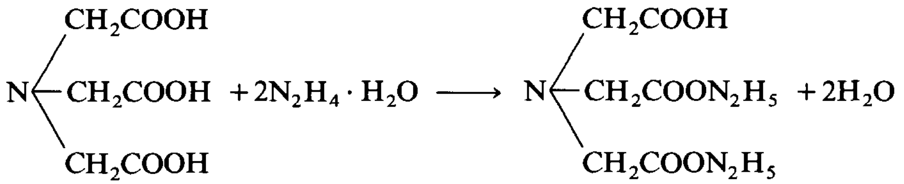
The IR spectrum of the compound was recorded using KBr pellets and a Perkin–Elmer 781 spectrophotometer. Simultaneous thermogravimetric–differential thermal analysis (TG–DTA) of the compound was recorded in air using an Ulvac Sinku–Riko TA 1500 instrument. The heating rate employed was 10 °C min^{-1}. Platinum cups were used as sample holders, and 5 mg of sample was used for the experiment.

RESULTS AND DISCUSSION

The reaction between NTA and hydrazine hydrate is exothermic and yields a colourless, highly hygroscopic compound. Chemical analysis of the product conforms to the formula $N(CH_2COO)_3H(N_2H_5)_2$ (found, N_2H_4 25.26%, C 29.1%; calculated N_2H_4 25.1%; C 28.23%).



$$N(CH_2COOH)_3 + 2N_2H_4 \cdot H_2O \longrightarrow N(CH_2COOH)(CH_2COON_2H_5)_2 + 2H_2O \tag{1}$$

Dihydrazinium nitrilotriacetate is readily soluble in water and can be re-precipitated by the addition of alcohol.

From the initial 1.91 g of NTA (0.01 mol) taken, the yield is found to be 2.642 g; this confirms the proposed formula for the salt.

The observed IR absorption frequencies of the salt, given in Table 1, also confirm the proposed formula. Typical absorptions of carboxylate and

TABLE 1

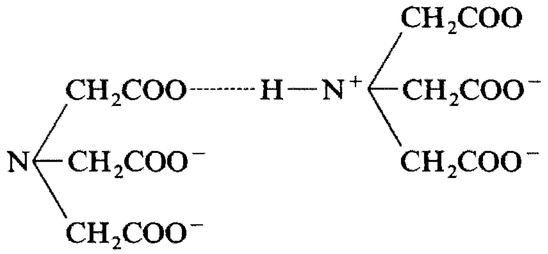
IR absorption frequencies of $N(CH_2COO)_3H(N_2H_5)_2$

cm^{-1}	Band assignment
3180 (Strong)	N–H stretching
3050 (Strong) 2840 (Strong)	C–H stretching of CH_2
1670 (Strong) 1625 (Strong)	COO asymmetrical stretching and hydrogen bonded carboxylate
1410 (Strong, sharp)	COO symmetrical stretching C–N stretching
1110 (Broad, strong)	NH_2 twisting and wagging
965 (Sharp, strong)	N–N stretching
915 (Sharp, strong)	C–C stretching
615 (Strong)	COO rocking

hydrazinium ions are seen in the spectrum. Absorptions at 1625 and 1670 cm^{-1} suggest [5]:

(i) the presence of only two of the three carboxylates as $-COO^-$;
(ii) the presence of hydrogen-bonded carboxylate, and
(iii) the acquisition of a positive charge by the nitrogen in NTA.

No absorption is detected at 1580 cm^{-1}, thus confirming the positive charge on the nitrogen. The two carboxylates, therefore, seem to be in ionic (negative) form, corresponding to the two $N_2H_5^+$. The third carboxylate attaches to the hydrogen atom through a hydrogen bond. Consequently the nitrogen in NTA is rendered positive owing to the H–N bond.



Absorption at 965 cm^{-1} has been assigned [6] to N–N stretching of $N_2H_5^+$ ion. Peaks at 1420–1400 cm^{-1} and 1625 cm^{-1} are found to be split. Similar observations have been made by Tomita and Ueno [5] for the nitrilotriacetate ions.

The dihydrazinium salt of NTA was heated in air to 600 °C to study its thermal properties. Whereas five peaks were observed in the DTA, the TG showed only four steps (Table 2). A sharp endotherm in the DTA with a maximum at 115 °C (Fig. 1) indicates a change of phase (melting) since no weight loss was detected in the TG.

The salt started losing weight above 130 °C. This decomposition is seen in the DTA as an endotherm over the temperature range 130–215 °C. This is

TABLE 2

Thermal analysis data of $N(CH_2COO)_3H(N_2H_5)_2$

Step no.	TG = temperature range (°C)	TG = weight loss (%)		DTA peak temperature (°C)	Reaction
		Found	Calc.		
1	–	–	–	115(–)	Melting
2	130–215	36.0	37.84	148(–)	Eqn (4)
3	240–310	74.0	75.29	262(–)	Decomposition of NTA
4	355–448	–	–	425(+)	Eqn (5)
5	448–585	100	100	535(+)	Eqn (6)

(–) Endothermic.
(+) Exothermic.

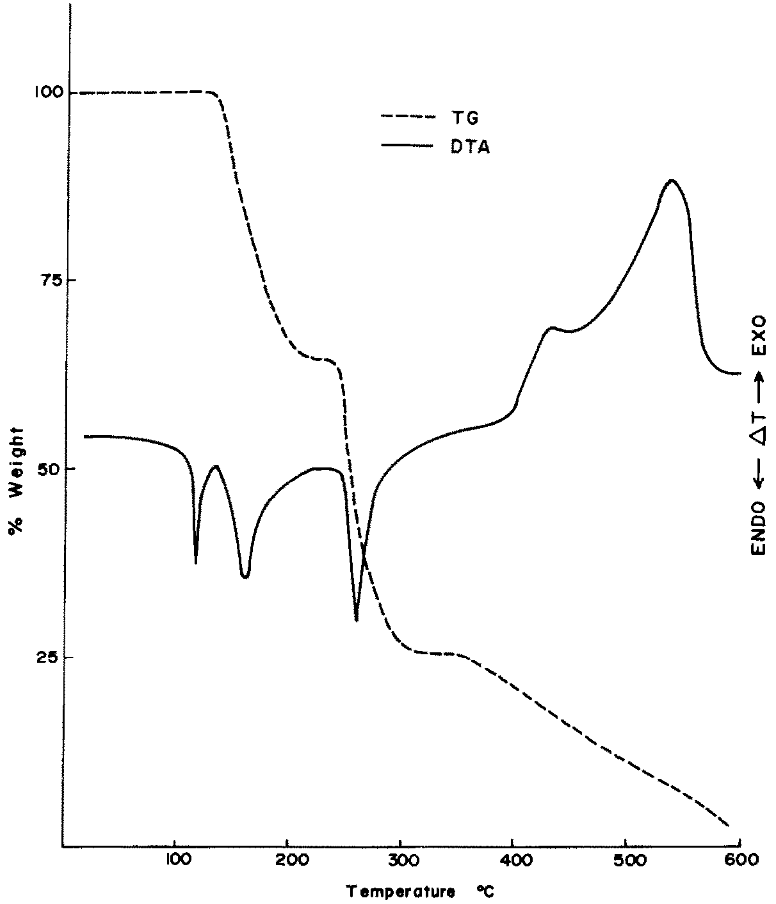


FIG. 1 TG and DTA of N (CH$_2$COO)$_3$ H(N$_2$H$_5$)$_2$

Fig. 1. TG and DTA of $N(CH_2COO)_3H(N_2H_5)_2$.

probably a result of dehydrazination. The reaction, in part, can be given as:

$$-COON_2H_5 \rightarrow -COOH + N_2H_4 \quad (2)$$

Subsequently, owing to partial decomposition of the salt, N_2H_4 probably yields $(N_2H_5)_2CO_3$:

$$2N_2H_4 + H_2O + CO_2 \rightarrow (N_2H_5)_2CO_3 \text{ or } 2N_2H_4 \cdot H_2CO_3 \quad (3)$$

The overall decomposition reaction in this first step can be written as:

$$2N(CH_2COO)_3H(N_2H_5)_2 \xrightarrow{\Delta} N(CH_2COO)_3H_3 + (N_2H_5)_2CO_3 + \text{gaseous products} \quad (4)$$

The observed weight loss of 36% in the first TG step conforms with the reaction. The residue after this step also tests positive for $N_2H_5^+$ and CO_3^{2-}.

DTA shows a further endotherm over the range 240–310 ° C, with a maximum at 262 ° C. This is because of the decomposition of the NTA produced in the previous step. These data are in good agreement with the reported [7] values for NTA.

The last two steps are exotherms (355–448 ° C and 448–585 ° C) and are continuous. The earlier exotherm appears as a shoulder to the latter. Hydrazinium salts are known [8,9] to decompose to their corresponding ammonium salts. Thus, hydrazinium carbonate $(N_2H_5)_2CO_3$ probably decomposes to $(NH_4)_2CO_3$ first, which, on further heating, decomposes to NH_3, H_2O and CO_2.

$$(N_2H_5)_2CO_3 \rightarrow (NH_4)_2CO_3 + N_2 + H_2 \qquad (5)$$

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2 \qquad (6)$$

NH_3 and CO_2 gases were qualitatively detected. The TG curve shows weight loss of 74% around 350 ° C. However, the last two steps can not be distinguished clearly on the TG curve as the weight loss is continuous up to 100%.

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