Thermochimica Acta 320 (1998) 115–120

thermochimica acta

Thermoanalytical properties of monobasic nitrilotriacetate salts of alkaline earth metals and zinc

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Received 2 August 1997; accepted 2 June 1998

Abstract

Monobasic metal nitrilotriacetate hydrated salts, $MH[N(CH_2COO)_3].xH_2O$, have been prepared by the reaction of nitrilotriacetic acid with metal carbonate. DTA studies of these salts both in N_2 and air reveal that these salts initially undergo dehydration and then, through acetate intermediates, decompose to oxycarbonates or oxides. © 1998 Elsevier Science B.V.

1. Introduction

Nitrilotriacetic acid, $N(CH_2COOH)_3$ or NTA, is a triprotic acid [1]. Like EDTA, it is an amino derivative of an organic acid and is known to co-ordinate with metal ion through both nitrogen and oxygen [2,3]. This acid has wide applications and important as a sequestrian agent in laundry detergents [4]. NTA removes hardness in water by complexation of Ca^{2+} and Mg^{2+} ions. It is common knowledge that the efficiency of the detergent solution is enhanced by elevated temperature. It is, therefore, important to know the effect of heat on the stability of the salts, Metal-NTA (M-NTA), produced in detergent solution.

M-NTA salts of the alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) and also Zn^{2+} were isolated as the solids and their thermonanalytical properties were investigated. These studies are presented here.

2. Experimental

Monobasic metal nitrilotriacetates, $MH[N(CH_2COO)_3]$, where M is Mg, Ca, Sr, Ba and Zn were prepared by warming aqueous suspension of MCO_3 and NTA and then isolating the product by crystallization [5].

Recrystallized salts were then characterized by chemical analysis [6,7] and the infrared (IR) spectral studies for conformity with those reported earlier [5,8].

Simultaneous TG-DTA was recorded using a NETZSCH STA – 409 Thermal Analyzer. A heating rate of $10\,K\,min^{-1}$ in N_2 atmosphere was used. Decomposition in air was also carried out but using a SHIMADZU THERMOBALANCE (Model TD-30) with a heating rate of $20\,K\,min^{-1}$. Powdered, 5–10 mg of sample was used in each experiment. Mass spectrometric analysis of the gaseous products of

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PII S0040-6031(98)00416-X

decomposition was carried out at the desired temperature in vacuum (10^{-8} torr) using an AEI MS-10 model instrument.

3. Results and discussion

Metal carbonates react with $N(CH_2COOH)_3$ to yield salts of the type $MH[N(CH_2COO)_3].xH_2O$, where M is Mg, Ca, Sr, Ba and Zn. The chemical analysis and the IR spectroscopic data were in good agreement with those reported in the literature [5]. General decomposition patterns for these salts in N_2 atmosphere can be summarised as follows.

On heating, these salts decompose in three or four steps. DTA and TG studies show initial endothermic dehydration at about 100°C, which occurs in a single or multiple steps depending upon the metal ion.

$$HM[N(CH_2COO)_3].xH_2O \rightarrow HM[N(CH_2COO)_3] + xH_2O \quad (1)$$

The anhydrous M-NTA salt on further heating decomposes endothermically to the corresponding metal acetate salt along with a large amount of gases viz. CO, H_2 and N_2. Mass spectrometry of the evolved gases, after decomposition of the Mg salt on heating to about 250°C, was carried out. The gases N_2 m/e=14.28; H_2O m/e=18; CO m/e=28 were detected along with lesser amounts of NH_3 m/e=17, thus supporting the proposed decomposition pattern. Generally, this decomposition reaction can be written as,

$$HM[N(CH_2COO)_3] \rightarrow M(CH_3COO)_2 + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 + 2CO \quad (2)$$

Traces of NH_3 vapours were also qualitatively detected when compounds were gradually heated in a tube.

The metal acetate, so formed, underwent further degradation when heated yielding mostly metal oxycarbonate as the residue. Acetone was (using 2,4 dinitrophenyl hydrazine) detected as one of the gaseous products. As metal acetates are known to decompose to give acetone in the vapour state, detection of acetone as one of the gaseous products further confirms the formation of metal acetate as an intermediate product in the metal nitrilotriacetate decomposition [9]. Moreover, metal acetates are known to form metal oxycarbonates on heating [9].

$$2M(CH_3COO)_2 \rightarrow xMO.yCO_2 + 2CH_3COCH_3 + (2-x)M + (2-x)CO_2 + (1-\tfrac{x}{2})O_2 \quad (3)$$

The values of 'x' and 'y' depend on the metal ion in the salt.

The decomposition of M-NTA to M-Acetate to M-oxycarbonate occurs in a short range of temperature. Both these steps are endothermic in nature. An exotherm observed between the two could be due to acetoxy free radical decomposition giving the gaseous products [10]. The last step (upto 700°C) is seen in the TG as a weight loss due to the reaction,

$$xMO.yCO_2 \rightarrow xMO.zCO_2 + (y-z)CO_2 \quad \text{where } z < y \quad (4)$$

This could be ascribed to a partial loss of CO_2 from the oxycarbonate resulting in the increase in $x:y$ ratio [11]. Decomposition of the individual salt is as given below.

3.1. TA of $HMg[N(CH_2COO)_3].3H_2O$

In N_2 atmosphere, this trihydrate salt of magnesium lost two H_2O molecules between 137–217°C. (Fig. 1). On further heating, the monohydrate salt decomposed to magnesium acetate in the range 222–389°C. Magnesium acetate, so formed, decomposed between 385–480°C, to its oxycarbonate [12]. The final residue at 620°C was MgO. Complementary peaks were observed in the DTA. (Table 1). Similar decomposition pattern (Fig. 3) was observed when this salt was heated in air to about 600°C.

3.2. TA of $HCa[N(CH_2COO)_3].2H_2O$

Calcium nitrilotriacetate dihydrate was stable upto 140°C. The decomposition of the salt, through partial dehydration was observed between 142–162°C with the weight loss of 3.6% indicating the loss of 0.5 H_2O. After further dehydration (175–219°C), the anhydrous calcium nitrilotriacetate decomposed (231–439°C) to calcium oxycarbonate $CaO.2CO_2$ with the weight loss of 45.1%. Between 439–668°C, the oxycarbonate was converted to $CaO.CO_2$ with the loss of 59.6% in weight, as seen in Fig. 2 [11].

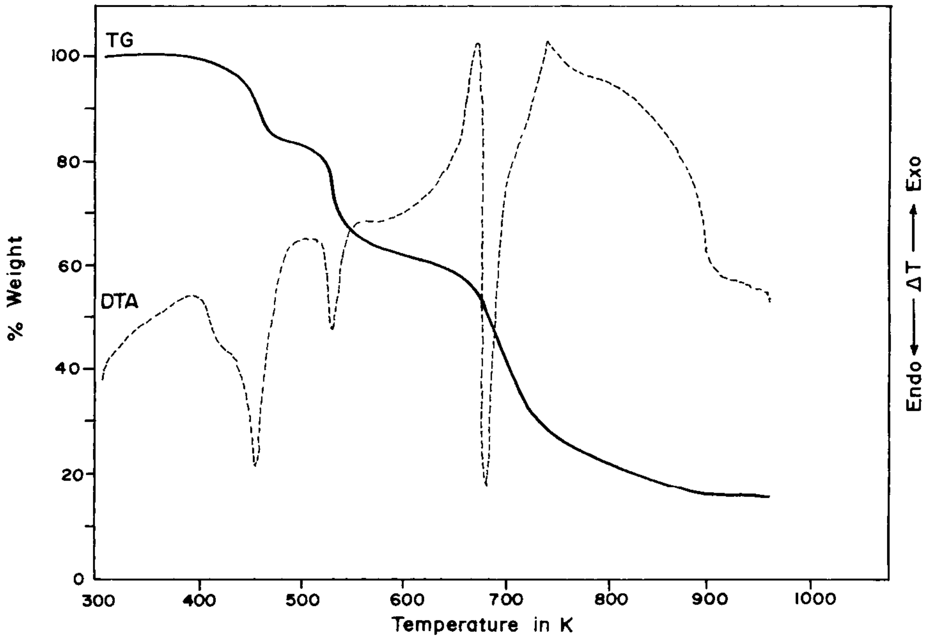

Fig. 1. TG, DTA of $HMg[N(CH_2COO)_3].3H_2O$.

Table 1
Thermal decomposition data of $HM[N(CH_2COO)_3]\cdot xH_2O$ in N_2 (10°C min^{-1})

	Step no.	Temperature range (°C)	Residue left	Weight loss (%)		DTA peak temperature (°C)
			$Y=N(CH_2COO)_3$	Observed	Calculated	
M=Mg	1	136.5–217	$HMgY.H_2O$	13.9	13.5	180.7(−)
x=3	2	222–384.6	$Mg(Ac)_2$	45.0	46.5	257.7(−)/392(+)
	3	384.6–480.1	$3MgO.2CO_2$	73.2	73.96	407(−)/473.1(+)
	4	481–620	3MgO	83.82	84.90	Broad
M=Ca	1	142.3–161.53	$HCaY.1.5H_2O$	3.6	3.4	150
x=2	2	175.0–219.23	HCaY	13.12	13.57	203.8
	3	230.8–290.38	–	–	–	–
	4	390.4–438.46	$CaO.2CO_2$	45.1	45.71	400(−)/426.9(−)
	5	439–665.38	$CaO.CO_2$	59.6	62.3	513(+)
M=Sr	1	142.3–194.2	$HSrY.2H_2O$	8.41	10.34	176.9
x=4	2	215–388	HSrY	21.1	20.69	Broad
	3	388.45–419.23	$Sr(Ac)_2$	39.7	40.91	396.15(−)/411.5(−)
	4	420–540	$SrO.2CO_2$	47.97	49.7	Broad
M=Ba	1	110–138.5	$HBaY.2H_2O$	4.9	4.7	131(−)
α=3	2	323.1–417.3	$Ba(Ac)_2$	30.0	32.87	389(−)
	3	417.3–520	$BaO.2CO_2$	35.8	36.55	493(−)
M=Zn	1	210–260	$HZnY.1.5H_2O$	3.16	3.19	246.2(−)
z=2	2	310–370	HZnY	13.16	12.78	357.7(−)
	3	380–435	$Zn(Ac)_2$	33.0	34.96	394.2(+)
	4	380–435	$ZnO.2CO_2$	44.21	39.34	419.2(+)
	5	435–560	$ZnO.CO_2$	56.31	55.56	Broad

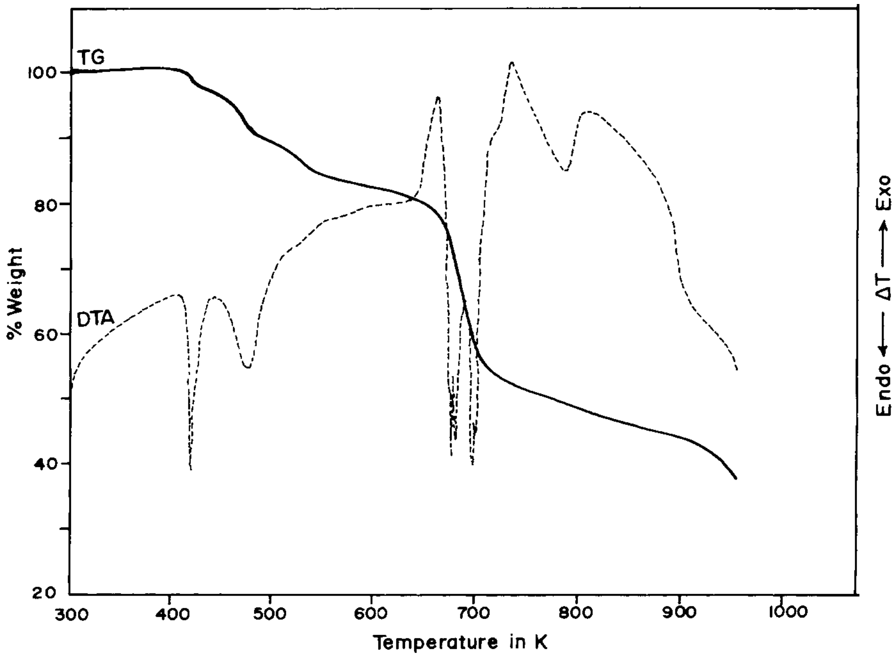

Fig. 2. TG, DTA of $HCa[N(CH_2COO)_3].2H_2O$.

Table 2
Thermogravimetric data of $HM[N(CH_2COO)_3].xH_2O$ in air (20°C min^{-1})

	Step no.	Temperature range (°C)	Residue left	Weight loss (%)	
			$Y=N(CH_2COO)_3$	Observed	Calculated
M=Mg	1	136.5–217.0	$HMgY.H_2O$	13.9	13.5
x=3	2	222–384.6	$Mg(Ac)_2$	45.0	46.5
	3	384.6–480.1	$3MgO.2CO_2$	73.2	73.96
	4	481–620	3MgO	83.82	84.90
M=Ca	1	140–160	$HCaY.1.5H_2O$	3.66	3.40
x=2	2	268–280	HCaY	12.6	13.57
	3	280–420	$Ca(Ac)_2$	40.5	40.43
	4	424–595	CaO	79.0	78.90
M=Sr	1	183–250	$HSrY.2H_2O$	8.40	10.34
x=4	2	260–419	$Sr(Ac)_2$	42.5	40.91
	3	419–600	$SrO.2CO_2$	49.43	49.70
M=Ba	1	370–438	–	–	–
x=3	2	438–570	BaO	60.3	59.31
M=Zn	1	30–130	$HZnY.1.5H_2O$	2.8	3.19
x=2	2	130–170	$HZnY.1.H_2O$	5.5	6.38
	3	170–250	$HZnY.0.5H_2O$	8.2	9.57
	4	250–330	HZnY	12.3	12.78
	5	390–495	ZnO	69.0	70.1

But when the same salt was heated in air (Table 2), although the first step was similar to the one observed in the N_2 atmosphere, the remaining steps were found to vary. Even the final residue was CaO (Fig. 3) instead of $CaO.CO_2$.

3.3. TA of $HSr[N(CH_2COO)_3].4H_2O$

The dehydration of this salt, containing four H_2O molecules, occurred in two steps in N_2 atmosphere. Initially, it lost two H_2O molecules between 142–194°C, followed by the remaining two molecules between 215–388°C. The weight loss in the two respective steps (Table 1) was 8.41% and 21.1% which could be attributed to the formation of anhydrous salt. When heated further, it decomposed to acetate with weight loss of 39.7% in the temperature range of 389–419°C. The weight loss in the last step indicated the formation of $SrO.2CO_2$, at 540°C [10]. Almost identical pattern of dehydration was observed when the salt was heated in air. The final residue at 580°C was similarly found to be oxycarbonate $SrO.2CO_2$.

3.4. TA of $HBa[N(CH_2COO)_3].3H_2O$

Barium nitrilotriacetate trihydrate on heating in N_2 atmosphere, lost one H_2O with the weight loss of 4.9% in the temperature range of 110–138°C. The dihydrate salt, so formed was stable upto 323°C. Beyond this temperature it further decomposed to $Ba(CH_3COO)_2$ and gaseous products as discussed earlier. The final residue at 700°C seems to be of oxycarbonate $BaO.2CO_2$ [13]. However, decomposition in air (Table 2) yielded BaO at 600°C.

3.5. TA of $HZn[N(CH_2COO)_3].2H_2O$

The salt of zinc (molecular weight=290.52) underwent dehydration in two steps. When heated in N_2 gas, $0.5H_2O$ (3.16% weight loss) and $1.5H_2O$ (13.16% weight loss) were lost in two stages (Table 1). Further decomposition, as observed in simultaneous TG-DTA, was similar to the other NTA salts. The sequence of decomposition being,

$$\text{Nitrilotriacetate} \rightarrow \text{Anhydrous} \rightarrow \text{Acetate} \rightarrow \text{Oxycarbonate}.$$

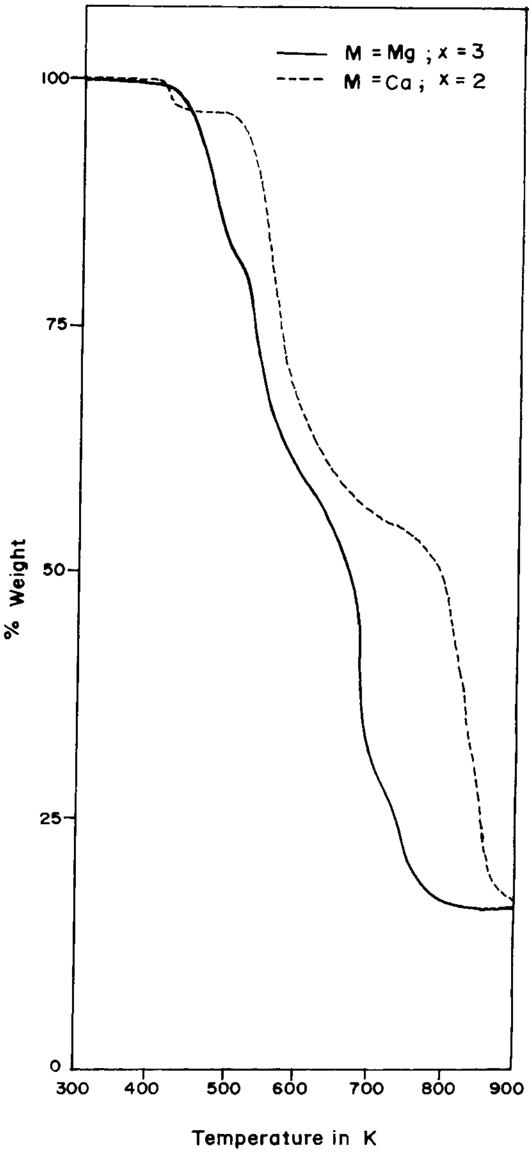

Fig. 3. TG of $HM[N(CH_2COO)_3].xH_2O$ in air.

However, when this salt was decomposed in air at an increased heating rate, the final residue in the TG was found to be ZnO.

Nitrilotriacetate salts of Ca and Mg are thus found to be stable below 100°C. Generally this type of salts decompose to metal oxycarbonates through acetates as intermediate steps.

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