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DTA and TG studies of zinc oxinate

O.G.Palanna

R and D Centre, RNS Institute of Technology, Channasandra, Bangalore-61, (INDIA)

Tel : 26483861

E-mail : drogp@hotmail.com

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ABSTRACT

An oxidative thermal decomposition of zinc oxinate is investigated through differential thermal analysis (DTA),Thermogravimetric (TG), Differential thermogravimetry(DTG), Infra-Red,(IR) and powder X-ray diffraction (XRD) techniques. The identification and the purity of zinc oxinate is carried out by IR spectrum of the sample. The hydrated zinc oxinate is $Zn(C_9H_6ON)_2 2H_2O$. The Differential thermal analysis pointed out that the sample is thermally stable between 25^0C and 125^0C. At 145^0C, it loses two molecules of water yielding anhydrous $Zn(C_9H_6ON)_2$. TG and DTG analysis showed that the anhydrous sample of oxinate is stable between temperatures 145^0C and 300^0C without weight loss. Further, the DTA, TG and DTG studies indicated that the oxidative thermal decomposition began above 300^0C, initially slowly with a loss of weight of the complex molecule; and the first phase is complete at 425^0C. The second exothermic peak is observed in the DTA curve at 560^0C which could be attributed to the elimination of residual organic part of the oxinate molecule with a considerable weight loss between 500^0C and 625^0C, as evident from TG curve of the sample. The final product of the oxidative thermal decomposition is ZnO at 625^0C and is stable, which is identified and characterized by XRD studies.

KEYWORDS

Oxidative;
Differential thermal analysis;
Oxinate;
Decomposition;
Exothermic;
Stable.

INTRODUCTION

In analytical chemistry, 8-hydroxy quinoline[1-3] (oxine) is used as one of the versatile reagents for the precipitation of number of cations as oxinates depending on the conditions of their synthesis. It is observed that oxine complexes with number of cations in neutral, ammoniacal or acetic acid-acetate buffered solutions to produce inner metal oxinates (Quinolates) of composition $M(C_9H_6ON)_n.xH_2O$, where M is the metal ion and 'n' is the valency of the cation..

There are several reports[4-11] on the investigation of the synthesis and characterization of metal oxinates and their associated thermal stability at various preparative procedures. Berg[6] synthesized Zinc oxinate of composition, $Zn(C_9H_6ON)_2 2H_2O$ in acid medium and is found to be stable below 72^0C. He further reports that yet another phase of composition $Zn(C_9H_6ON)_2$ $1.5H_2O$ existed at 100^0C, which gets dehydrated at $120\text{-}130^0$C. Fleck and ward[5] could synthesize zinc

oxinate phase at pH between 4.6 and 13.0 and found that this is stable between 110 -160^{0}C. Charles and Langer[6] have investigated thermal stability and volatilization of zinc oxinate in vacuum. Borrel and Paris[7-9] have prepared zinc oxinate by dissolving zinc salt and ammonium acetate buffer at pH 7.0 by adding requisite quantity of oxine, which is dissolved in acetic acid. Borrel and Paris have used conventional Chevanard thermobalance and have observed that the $Zn(C_9H_6ON)_2 2H_2O$ phase (Zn content: 16.66% per mole molecule of Zinc oxinate) is stable up to 72^{0}C and changes to anhydrous phase(Zn content: 18.43%), $Zn(C_9H_6ON)_2$, at 170^{0}C.They have reported that the initiation of decomposition started at 305^{0}C and gave ZnO at 700^{0}C as the final product.

Recently, the study of solid oxinate complex of few metals have been investigated by C.A Ribeiro and others[11]. In the DTA curve ,they observed endothermic peaks at 92, 132, 181^{0}C; and a small kink at 370^{0}C. A huge exothermic peak at 550-560^{0}C. The TG curve of the sample in N_2 atmosphere indicated a weight loss at 141^{0}C and also at 192^{0}C due to two step dehydration process. The oxidative decomposition took place in the presence of N_2 is between 320^{0}C and 512^{0}C with loss of weight. An intense peak at 370^{0}C is attributed to the fusion and the second broad peak at 455^{0}C , partial volatilization of the anhydrous oxinate molecule.

It is clear from earlier reports[4-11] that ambiguity still persists in the investigation of zinc oxinate. This has prompted to reinvestigate the zinc oxinate and subjected to DTA,TG and DTG analysis in air to elicit out the thermal stability and oxidative decomposition of sample.

EXPERIMENTAL

A pure sample of zinc oxinate is obtained by adopting the procedure as given: 1:2 molar quantities of analytical grade Zinc salt and 8-hydroxy quinoline are used to precipitate zinc oxinate at pH 4.4. 25 ml of 0.1M zinc salt(containing 0.163g of Zn) is taken with 100ml acetic- acetate buffer solution(145ml of 1M acetic acid + 50 ml of 1M NaOH in 500ml of distilled water) mixture, heated for to 7- 80^{0}C for 2 -3 minutes.25ml of 0.2M oxine solution(containing 0.7255 g of oxine dissolved in 2M acetic acid) is added to the hot solution with constant agitation. The pH of the solution is maintained at pH =4.4. The precipitate is allowed to settle, filtered and washed several times with warm water to remove the soluble impurities. A pale green colored precipitate of zinc oxinate is dried in hot air oven at 110^{0}C and kept in a desicator.

The following techniques have used to study the thermal decomposition of solid complex, zinc oxinate, using DTA ,TG and DTG(Mettler TA 4000). XRD pattern and infra–Red spectroscopy were used for identification and the characterization of the complex and the residue of the thermal decomposition. The investigation is carried out with following conditions (i) heating rate,10^0 /minute ii) atmosphere, air iii) amount of zinc oxinate taken : 5.4720mg and temperature range: 25 - 800^{0}C.

RESULTS AND DISCUSSION

The absence of IR spectrum characteristic of oxine molecule in zinc oxinate aggregates showed that the synthesized nickel oxinate is pure. The DTA of zinc oxinate (figure 1) is recorded in an atmosphere of air between 25-800^{0}C. There is no fusion/ volatilization peaks of oxine in DTA curve. The first endothermic peak at 145^{0}C in the DTA curve (figure 1) is observed. It is evident that the chelate complex of zinc obtained under the conditions of preparation is quite stable up to about 125^{0}C. Two other exothermic peaks are also noticed at 425^{0}C and 560^{0}C in the DTA curve. These peaks, especially, the one at 560^{0}C is huge one indicating possibly the decomposition of the complex molecule, which is highly exothermic The initial exothermic peak begins at about 300^{0}C and ends up at 425^{0}C,

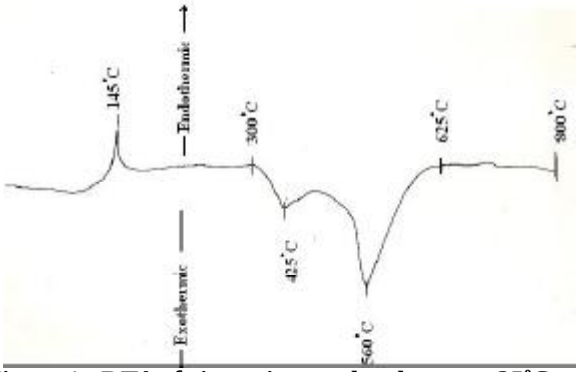

Figure 1 : DTA of zinc oxinate taken between 25^{0}C and 800^{0}C in air

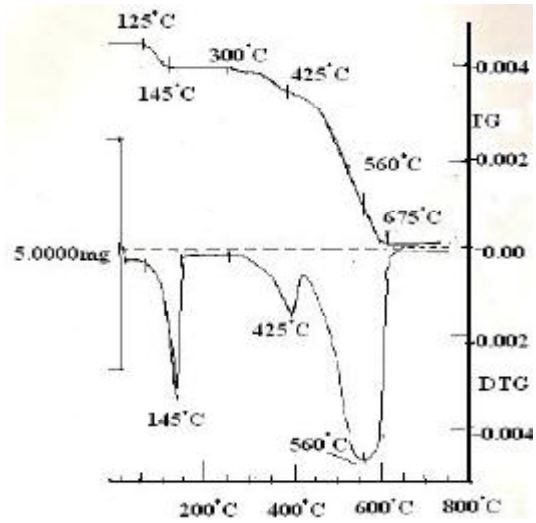

Figure 2 : TG and DTG results of zinc oxinate between 25^{0}C andf 800^{0}C in air

which may be due to thermal elimination of a part of the complex molecule. A huge exothermic reaction due oxidative thermal decomposition begins at about 500^{0}C and is complete at 625^{0}C with a maximum peak positioned at 560^{0}C. At 625^{0}C ,the final product obtained is ZnO. The XRD pattern characteristic of pure ZnO is obtained(ASTM Card file No 5-0664).

The results of DTA is supported by results of both Therrmogravimetric (TG) analysis and differential thermogravimetry (DTG) of zinc oxinate (figure 2). The TG curve showed the first weight loss is between 125^{0}C and 145^{0}C (figure 2); and the second weight loss between 300^{0}C and 425^{0}C; and finally, major weight loss is between 500^{0}C and 560^{0}C. The weight loss in TG curve behavior with increase of temperature is corroborated by the results of DTG, which clearly indicated corresponding peaks at 145^{0}C , 425^{0}C and 560^{0}C which is due to the elimination of water molecules and the complex process of oxidative thermal decomposition of zinc oxinate. A nearly flat region of the TG and DTG curves (Figure 2) showed that the hydrated zinc oxinate ,$Zn(C_9H_6ON)_2 2H_2O$, is thermally stable between 25 -125^{0}C with Zn content at 16.77% per mole. The observed weight loss at 145^{0}C is 9.34% which is supported by DTG peak at 145^{0}C, is attributed to the elimination of two water molecules from the hydrated sample [$Zn(C_9H_6ON)_2 2H_2O$]. DTA result confirms the result indicating that the elimination of water is an endothermic process at 145^{0}C. This weight loss in the TG curve amounts to a loss of exactly 36.00 g/mole.As a result of removal of water hydration , the Zn content per mole of oxinate raises to 18.48. The anhydrous $Zn(C_9H_6ON)_2$ is stable between temperature 145^{0}C-300^{0}C. Both the TG and DTG curves (figure 2) indicate that initiation reaction of thermal oxidative degradation process of oxinate sets in above 300^{0}C, which is further supported by the exothermic DTA curve between 300 and 425^{0}C (figure 1). A part of the complex molecule is eliminated (79.0g per mole) between these temperatures increasing the percentage of zinc per mole to 21.05% and hence it not due fusion process. A rapid oxidative thermal degradation process of Zinc oxinate with an exothermic reaction begins at 500^{0}C and completed at 625^{0}C(DTA peak at 560^{0}C), which accounts for the entire decomposition of the chelated oxinate molecule yielding the final residue, ZnO. The TG and DTG results also confirms this process of decomposition of oxinate molecule commenced at 500^{0}C and ended at about 625^{0}C with a maximum weight loss 52% per mole of oxinate (i.e., 202.6 g/mole between 425^{0}C and 560^{0}C) and the Zn content has raised to 34.94%. Palanna and others have noticed in their earlier studies that there is no abrupt breaking of bond or fusion or volatilization of complex molecule of any metal oxinate complex on heating up to about 300^{0}C; but it is found, ultimately, the complex molecule decomposes, as is evident from TG and DTG curve (figure 2) ; and the weight loss observed between 145 and 625^{0}C is 272.38g/mole [i.e., $(C_9H_6ON)_2$ part of oxinate =288.32 – O = 288.32 -16.0 = 272.32g.].

The final product obtained above 625^{0}C is ZnO, which is indentified and characterized by powder XRD technique. The percentage zinc in the final product ,ZnO, is 80.40. The data of TG and DTG results of the thermal degradation of $Zn(C_9H_6ON)_2 2H_2O$ are given in TABLES 1 and 2.

Concluding it can be remarked that

1. Pure zinc oxinate, $Zn(C_9H_6ON)_2 2H_2O$, can be synthesized at pH = 4.4.
2. Hydrated zinc oxinate phase is stable between 25 - 125^{0}C, while the anhydrous phase is stable between 145^{0}C and 300^{0}C.
3. A quantitative estimation of Zn as ZnO is possible above 625^{0}C using oxine as precursor for the precipitation as zinc oxinate.

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TABLE 1 : Thermogravimetric (TG) data of $Zn(C_9H_6ON)_2 2H_2O$ (Weight of $Zn(C_9H_6ON)_2 2H_2O$ taken : 5.4720 mg, Mol.weight of $Zn(C_9H_6ON)_2 2H_2O$ = 389.68)

Temperature Range in DTG curve ^{0}C	DTG peak temperature ^{0}C	Total weight loss corresponding to DTG peak	Weight loss per mole of oxinate (g)	Percentage weight loss between the DTG peaks	Percentage of total weight loss per mole oxinate
25-145	145	0.5055	36	9.24	-
300 – 425	425	1.1240	80.0	10.86	20.52
425 -560	560	2.8450	202.60	32.00	52.00
560 - 625	625	4.3304	308.38	27.14	79.14
Total weight loss of sample at 625^{0}C		4.3304	308.38	-	79.14
Weight of the residue,ZnO		1.1416	81.30		20.86
Total		5.4720	389.68	-	100

TABLE 2 : TG analysis data of $Zn(C_9H_6ON)_2 2H_2O$

DTG peak temperature ^{0}C	Weight loss per mole of oxinate (g)	Weight calculated from TG curve (g)/mole	Percentage of Zn in the thermal product theoretical	experimental
25-125	-	389.68	16.77	16.77
145	36	353.68	18.48	18.48
425	80.00	309.68	-	21.00
560	202.60	187.08	-	34.94
625	308.38	81.30	80.00	80.0*

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