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THERMAL BEHAVIOUR OF 8-HYDROXYQUINOLINE COMPLEXES WITH NICKEL(II)/COPPER(II)/ZINC(II) HYDROXIDES

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Abstract

Thermal behaviour of $M(OH)_2(8\text{-}HQ)_2$ (M=Ni, Cu and Zn; 8-HQ=8-hydroxyquinoline) has been studied by dynamic TG and DTA methods in nitrogen atmosphere. The percent weights lost in different temperature range was calculated from TG curves. The mode of decomposition has been supported by endotherms observed in DTA curves of the respective compounds.

Keywords: complexes, DTA, TG

Introduction

In our previous papers [1, 2] we have reported the formation of $M(OH)_2(8\text{-}HQ)_2$ by solid state reaction between $M(OH)_2$ (M=Ni, Cu and Zn) and 8-hydroxyquinoline (8-HQ). The composition of these compounds has been decided by their metal contents and elemental analysis data. Analysis of powder X-ray diffraction patterns has revealed that these compounds are single phased new compounds and differ from usual metal(II) oxinates [$M(C_9H_6OH)_2$; M=Ni, Cu and Zn] formed from M^{2+} ions and 8-HQ reactions in solution phase. IR spectral data have shown that 8-HQ acts as a monodentate ligand in solid state with nitrogen atom being the only co-ordination site. This unique behaviour of 8-HQ in solid state is in contrast to its behaviour in solution phase in which it acts as a strong bidentate ligand with nitrogen as well as oxygen atoms as the coordination sites. Thermal behaviour of metal(II) oxinates formed from reactions of M^{2+} (aq) and 8-HQ (solution) has been investigated by previous workers [3–7]. Metal(II) hydroxides [$M(OH)_2$; M=Ni, Cu and Zn] are known to have layered structures [8] possessing HO–M–OH layers held together by weak Van der Waals' forces. These weakly linked layers are flexible and inter layer spacing is subject to change on intercalation of organic molecules in the inter layer space available in the crystal structure [9]. The formation of $M(OH)_2(8\text{-}HQ)_2$ by solid state reaction between $M(OH)_2$ and 8-HQ seems to be facilitated by the intercalation of 8-HQ molecules in the inter layer space available in the crystal structure of $M(OH)_2$. The intercalated 8-HQ molecules would escape out on heating. In order to ascertain this aspect, the present investigation has been undertaken. In this paper the thermal behaviour of [$M(OH)_2(8\text{-}HQ)_2$; M=Ni, Cu and Zn] in the

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temperature range 50–900°C using dynamic TG and DTA methods has been reported. The experiments were carried out in nitrogen atmosphere.

Experimental

$M(OH)_2(8\text{-}HQ)_2$ were prepared by solid state reaction between $M(OH)_2$ (M=Ni, Cu and Zn) and 8-HQ as reported earlier [1, 2]. The composition of these compounds was checked by metal estimation using standard gravimetric methods (nickel as nickel(II) dimethylglyoximate [10], copper as copper(I) thiocyanate [10] and zinc as zinc(II) oxinate [10].

TG and DTA curves of solid state reaction products (Figs 1–6) have been obtained (RSIC, Nagpur, India) using a Perkin-Elmer thermal analyser in nitrogen atmosphere from ambient to 900°C at heating rate 10°C min^{-1}.

Results and discussion

The values of percent weight lost (Table 1) in different temperature range has been computed from the TG curves (Figs 1–3). The data indicate that $Ni(OH)_2(8\text{-}HQ)_2$ undergoes thermal decomposition in three steps as shown below:

$$Ni(OH)_2(8\text{-}HQ)_2 \xrightarrow{60-180^\circ C} Ni(OH)_2(8\text{-}HQ) + 8\text{-}HQ \qquad (1)$$

$$Ni(OH)_2(8\text{-}HQ)_2 \xrightarrow{180-210^\circ C} NiO(8\text{-}HQ) + H_2O \qquad (2)$$

$$NiO(8\text{-}HQ) \xrightarrow{210-398^\circ C} NiO + 8\text{-}HQ \qquad (3)$$

The percent weight remaining after TG experiment is in agreement with calculated value of nickel(II) oxide. It is seen from Fig. 1 that the mass loss (~36.6%) is fast up to 140°C. Above this temperature the mass loss becomes slow and it is over up to 180°C. The temperature of oxide formation is ~398°C and the mass of the residue (NiO) remains constant up to 840°C. Data given in Table 1 indicate that $Zn(OH)_2(8\text{-}HQ)_2$ undergoes thermal decomposition in a manner different from that of $Ni(OH)_2(8\text{-}HQ)_2$ as given below.

$$Zn(OH)_2(8\text{-}HQ)_2 \xrightarrow{100-183^\circ C} ZnO(8\text{-}HQ)_2 + H_2O \qquad (1)$$

$$ZnO(8\text{-}HQ)_2 \xrightarrow{184-403^\circ C} ZnO(8\text{-}HQ) + 8\text{-}HQ \qquad (2)$$

$$ZnO(8\text{-}HQ) \xrightarrow{404-750^\circ C} ZnO + 8\text{-}HQ \qquad (3)$$

The percent weight remaining after the TG experiment is again in agreement with calculated value of the zinc(II) oxide. In this case the temperature of oxide formation ~750°C and no further mass loss is observed up to 900°C. The mode of thermal decomposition of $Cu(OH)_2(8\text{-}HQ)_2$ is very much similar to that of $Zn(OH)_2(8\text{-}HQ)_2$ as shown below:

$$\mathrm{Cu(OH)_2(8\text{-}HQ)_2} \xrightarrow{170-225^{\circ}\mathrm{C}} \mathrm{CuO(8\text{-}HQ)_2} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{CuO(8\text{-}HQ)_2} \xrightarrow{226-380^{\circ}\mathrm{C}} \mathrm{CuO(8\text{-}HQ)} + \mathrm{8\text{-}HQ} \tag{2}$$

$$\mathrm{CuO(8\text{-}HQ)} \xrightarrow{380-660^{\circ}\mathrm{C}} \mathrm{CuO} + \mathrm{(8\text{-}HQ)_{1-x}} + \mathrm{x(8\text{-}HQ)} \quad (x=0.73) \tag{3}$$

However, the percent weight remaining after the TG experiment up to 900°C is higher than that calculated for copper(II) oxide. From this it can be suggested that under the temperature range of experiment (up to 900°C) the cooper compound does not decompose completely.

The modes of thermal decomposition as discussed above are supported by the DTA curves (Figs 4–6) of respective compounds. In the case of $\mathrm{Ni(OH)_2(8\text{-}HQ)_2}$, two endothermic peaks are observed in its DTA curve (Fig. 4). The first endotherm in the temperature range 60–220°C with a minimum at 115°C is comparatively broad than the second one. This may be due to the first and second step thermal de-

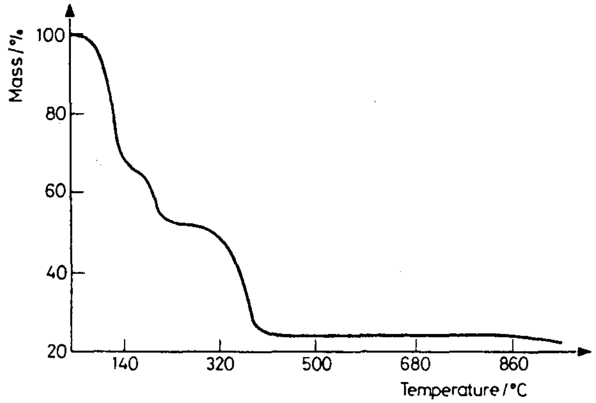

Fig. 1 TG curve of $\mathrm{Ni(OH)_2(8\text{-}HQ)_2}$

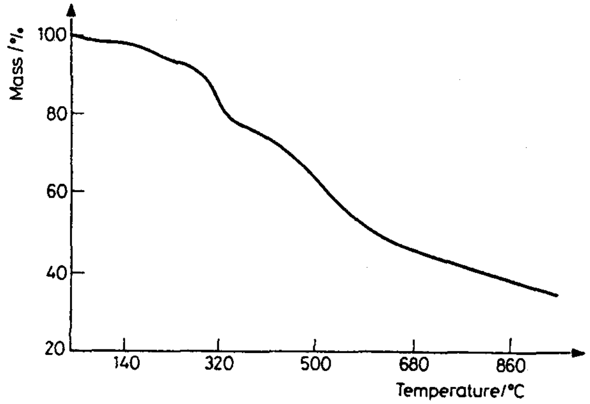

Fig. 2 TG curve of $\mathrm{Cu(OH)_2(8\text{-}HQ)_2}$

Table 1 Thermal decomposition data

Composition	DTA results		TG results				
	T_{peak}/°C	T_{range}/°C	Mass loss/% found calc.	T_{range}/°C	Loss of	Composition of the residue	$T_{oxide\ formation}$/°C
$Ni(OH)_2(8\text{–}HQ)_2$	115.0	60–220	36.6 (37.8)	60–180	8–HQ	NiO	398
	326.4	253-400	4.3 (4.69)	180–210	H_2O		
			35.3 (37.9)	210–398	8–HQ		
$Cu(OH)_2(8\text{–}HQ)_2$	210.9	180–240	4.4 (4.67)	170–225	H_2O		
	273.9	240–340	37.0 (37.4)	226–380	8–HQ		
	433.4	395–510	29.4 (37.4)	380–660	x(8–HQ) (x=0.73)	CuO	900
$Zn(OH)_2(8\text{–}HQ)_2$	130.0	90–170	4.2 (4.61)	100–183	H_2O	–	–
	187.8	171–344	36.6 (37.2)	184–403	8–HQ		
	358.6	345–585	35.1 (37.2)	404–750	8–HQ	ZnO	750

composition undergone by the compound. The second endothermic peak in the temperature range 253–400°C with a minimum at 326.4°C may be due to the third step decomposition. The three-step thermal decomposition of $Zn(OH)_2(8\text{-}HQ)_2$ is supported by three endotherms (Fig. 6) in its DTA curve. The first endothermic peak in the temperature range 90–170°C with a minimum at 130°C seems to be due to the loss of one H_2O molecule. The second endothermic peak in the temperature range 171–344°C with a minimum at 187.8°C is due to the loss of one 8-HQ molecule. The third endothermic peak in temperature range 345–585°C with a sharp minimum at 358.6°C may be due to loss of remaining 8-HQ molecule. The three-step thermal decomposition undergone by $Cu(OH)_2(8\text{-}HQ)_2$ is also supported by the three endotherms observed in its DTA curve (Fig. 5). The first peak observed in temperature range 180–240°C with a minimum at 210.9°C is due to loss of H_2O molecule as shown in the step (1). The second endotherm in the temperature range 240–340°C with a minimum at 273.9°C confirms the loss of one 8-HQ molecule

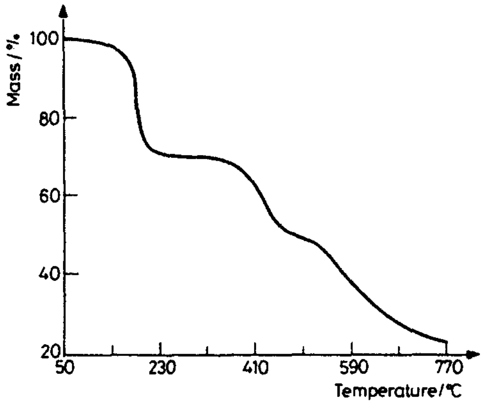

Fig. 3 TG curve of $Zn(OH)_2(8\text{-}HQ)_2$

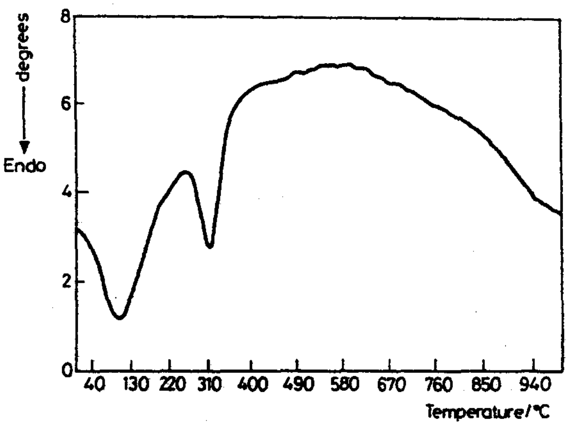

Fig. 4 DTA curve of $Ni(OH)_2(8\text{-}HQ)_2$. Scan rate: 10°C min^{-1}

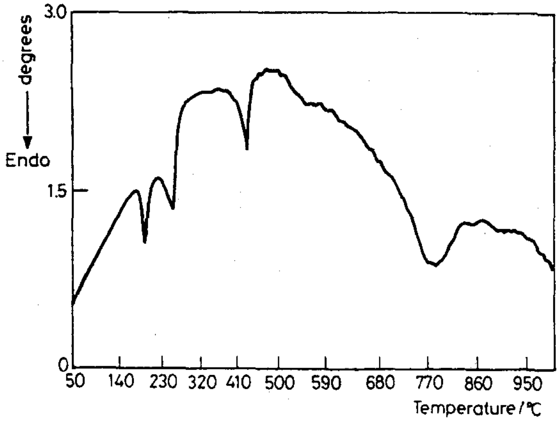

Fig. 5 DTA curve of $Cu(OH)_2(8\text{-}HQ)_2$. Scan rate: 10°C min^{-1}

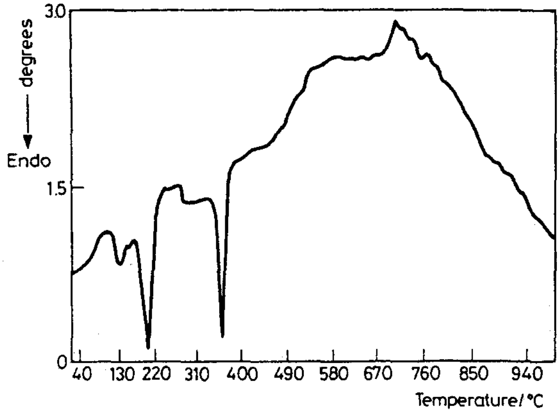

Fig. 6 DTA curve of $Zn(OH)_2(8\text{-}HQ)_2$. Scan rate: 10°C min^{-1}

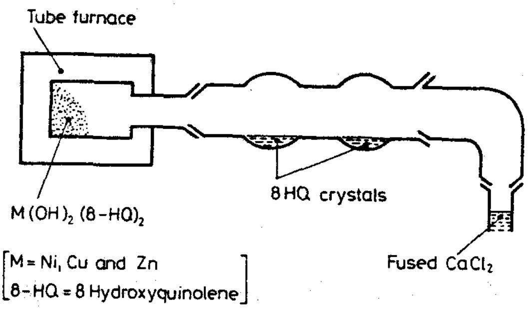

Fig. 7 Experimental setup for testing of formation of 8-HQ on heating

shown in step (2). The third endotherm in the temperature range 395–510°C with a minimum at 433.4°C is due to incomplete decomposition (step 3). The evolution of 8-HQ has been confirmed by heating these compounds in a tube furnace at (200±1°C) in an experimental set up (Fig. 7) made up of corning glass. Shining white crystals of 8-HQ (*mp*=75°C) were condensed in the glass tube outside the furnace.

On the basis of these observations it can be concluded that the solid state reaction products [$M(OH)_2(8\text{-}HQ)_2$; *M*=Ni, Cu and Zn] are formed by the intercalation of 8-HQ molecules in the inter layer space available in crystals of metal(II) hydroxides [$M(OH)_2$; *M*=Ni, Cu and Zn]. These intercalated 8-HQ molecules escape out on heating. Thus our contention, that these compounds [1, 2] are different from metal(II) oxinates [$M(C_9H_6ON)_2$; *M*=Ni, Cu and Zn] formed from reactions in solution phase, is correct.

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