Thermochimica Acta, 195 (1992) 1–4
Elsevier Science Publishers B.V., Amsterdam

Thermal studies on [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]copper(II) · $0.25H_2O$

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(Received 13 March 1991)

Abstract

The thermal decomposition progression and the kinetics of non-isothermal decomposition of [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]Cu(II)$0.25H_2O$) are presented.

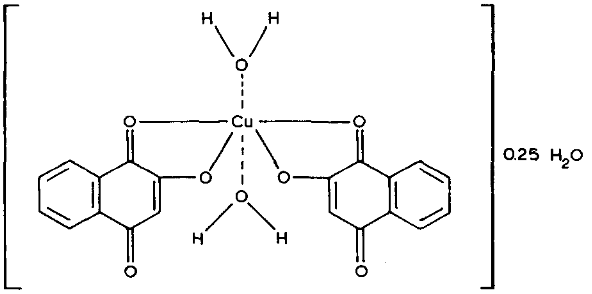
INTRODUCTION

A considerable amount of work has been done on hydroxynaphthalenedione [1–8].

We have prepared [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]-Cu(II)$0.25H_2O$ and studied its thermal dissociation kinetically following Dave and Chopra (DC) [9] and Coats and Redfern (CR) [10] methods.

EXPERIMENTAL

All the chemicals used were of Analar grade. The slow addition of copper ions (aqueous phase) to the sodium salt of 2-hydroxy-1,4-naphthalenedione (Aldrich Co., USA) with constant stirring resulted in a brown precipitate of metal chelate which, from elemental analysis, was of composition $[Cu(C_{10}H_5O_3)_2 \cdot 2H_2O]0.25H_2O$.



Scheme 1. [Diaqua bis(2-hydroxy-1,4-naphthalenedionato)]Cu(II)$0.25H_2O$.

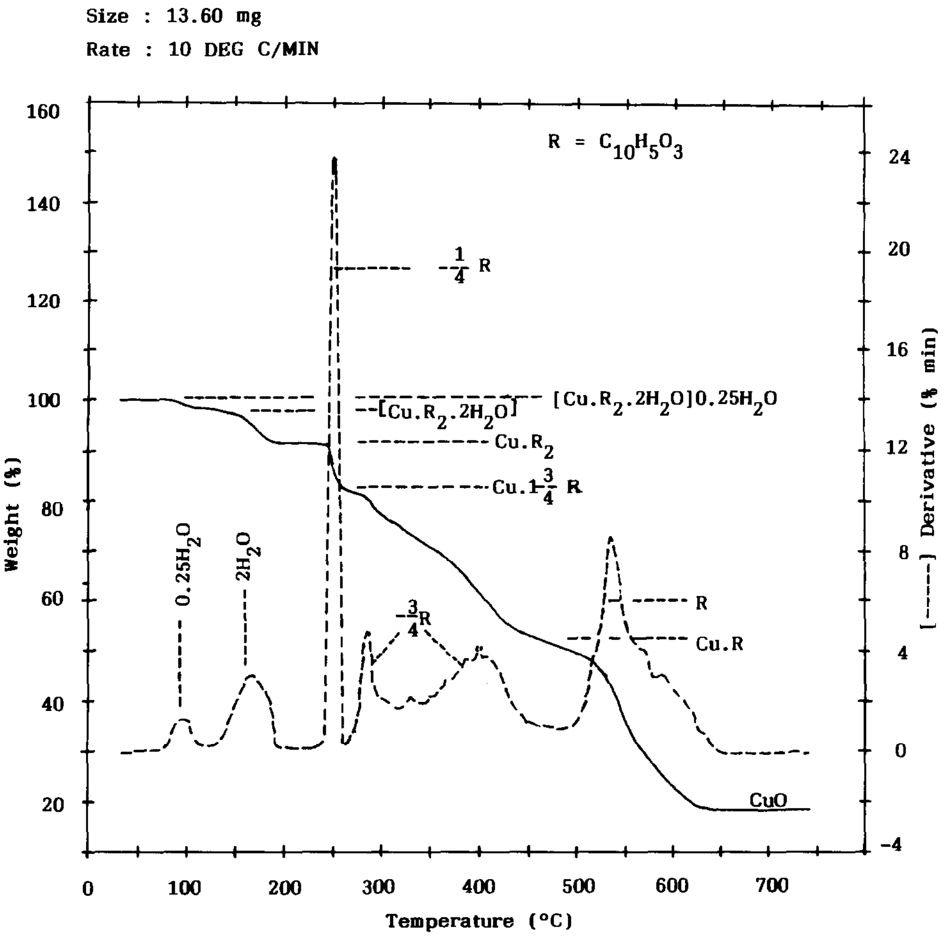


Fig. 1. TG and DTG curves of [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]Cu(II)· $0.25H_2O$ recorded on a Du Pont 1090.

The metal chelate was pyrolysed using a Du Pont 1090; Fig. 1 shows the TG/DTG curves.

RESULTS AND DISCUSSION

The copper-2-hydroxy-1,4-naphthalenedione chelate as ascertained thermally has the notation [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]-Cu(II), with $0.25H_2O$ as lattice water (Scheme I).

From Fig. 1 it is clear that the copper chelate is thermally stable up to 90 ° C. The lattice water ($0.25H_2O$) was lost up to 100 ° C; then there is a level portion on the curves up to 145 ° C, corresponding to a definite species, diaqua bis(2-hydroxy-1,4-naphthalenedionato)Cu(II). As the temperature increased over 145 ° C, more of the coordinated water molecules were lost; up to 185 ° C, the loss of $2H_2O$ was complete, with formation of

TABLE 1

Pyrolysis data for [diaqua bis(2-hydroxy-1,4-naphthalenedionato)Cu(II)]·$0.25H_2O$

Stable phase (temp. range) (°C)	Loss	Loss (%)		CuO (%)	
		Found	Calc.	Found	Calc.
$[CuR_2 \cdot 2H_2O]0.25H_2O$ (90)	–	–	–		
$CuR_2 \cdot 2H_2O$ (100–145)	$0.25H_2O$	1.00	0.95		
CuR_2 (185–245)	$2H_2O$	9.00	9.00		
$CuR_{1.75}$ (255–285)	0.25R	19.00	18.30		
CuR (450–520)	0.75R	49.00	47.44		
CuO (630 onwards)	R	81.00	84.55	19.00	17.67

$R = C_{10}H_5O_3$.

anhydrous bis(2-hydroxy-1,4-naphthalenedionato)Cu(II) (plateau, 185–245 °C). From 245 to 255 °C, 0.25R (where R is $C_{10}H_5O_3$) was lost leaving a new species of composition $CuR_{1.75}$ (plateau, 255–285 °C), which lost a further 0.75R in the temperature range 285–450 °C. The plateau (450–520 °C) coincided with CuR, which became CuO with the loss of the remaining R molecule from 520 to 630 °C.

$$\underset{\mathbf{I}}{[CuR_2 \cdot 2H_2O]\,0.25H_2O} \xrightarrow[-0.25H_2O]{90\text{–}100\,^\circ C} \underset{\mathbf{II}}{CuR_2 \cdot 2H_2O} \xrightarrow[-2H_2O]{145\text{–}185\,^\circ C} \underset{\mathbf{III}}{CuR_2} \xrightarrow[-0.25R]{245\text{–}255\,^\circ C}$$

$$\underset{\mathbf{IV}}{CuR_{1.75}} \xrightarrow[0.75R]{285\text{–}450\,^\circ C} \underset{\mathbf{V}}{CuR} \xrightarrow[-R]{520\text{–}630\,^\circ C} \underset{\mathbf{VI}}{CuO}$$

where $R = C_{10}H_5O_3$.

Table 1 shows the pyrolysis data for [diaqua bis(2-hydroxy-1,4-naphthalenedionato)]Cu(II)$0.25H_2O$.

The thermogram (Fig. 1) has five sigmoids, indicating five solid state reactions with **I**, **II**, **III**, **IV**, **V** and **VI** being stable phases. These reactions have been analysed kinetically using eqns. (1) and (2), Dave and Chopra (DC) [9], or eqn. (3), Coats and Redfern (CR) [10].

$$k = \frac{(A/m_0)^{n-1}(-dx/dt)}{(A-a)^n} \tag{1}$$

For $n = 1$, this reduces to

$$K = \frac{(-dx/dt)}{(A-a)} \tag{2}$$

where $-dx/dt$ (deviation from baseline), A (total area) and a (area at time t under DTG curves) were estimated from the DTG traces (Fig. 1).

The Coats and Redfern equation is

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) = \log\frac{AR}{aF}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3RT} \tag{3}$$

For $n = 1$, a plot of $\log[\ln(1-\alpha)]/T^2$ against $1/T$ should result in a line of slope $E/2.3R$ for the correct value of n [10].

The reactions, resembling the type A(s) → B(s) + C(g), on which different mathematical treatments have been tested and verified [11], see below, follow first-order kinetics ($n = 1$).

$\mathbf{I} \rightarrow \mathbf{II} + 0.25H_2O$

$n = 1,\ E = 173.89$ kJ mol^{-1} (DC)

$\mathbf{II} \rightarrow \mathbf{III} + 2H_2O$

$n = 1,\ E = 186.51$ kJ mol^{-1} (DC)

$n = 1,\ E = 108.39$ kJ mol^{-1} (CR)

$\mathbf{IV} \rightarrow \mathbf{V} = 0.75R$

$n = 1,\ E = 52.39$ kJ mol^{-1} (CR)

$\mathbf{V} \rightarrow \mathbf{VI} + R$

$n = 1,\ E = 1153.03$ kJ mol^{-1} (CR)

The E values are shown with the method employed in parentheses. **I**, **II**, **III**, **IV**, **V** and **VI** are the stable phases obtained at different stages. The reaction **III** → **IV** + 0.25R was too fast to be studied.

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