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Kinetics of the Thermal Decomposition of Cu (II) Complex of 8 - Hydroxy Quinoline-5 Sulphonic Acid

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ABSTRACT

The thermal properties of copper (II) 8- hydroxy quinoline -5 sulphonic acid has been investigated. The thermal decomposition occurs in three stages. All the three stages of decomposition follow one after the other without any stable compound in between showing that the complex is volatile. The kinetics of the thermal decomposition of the complex has been studied using thermogravimetry (TG) in conjunction with DTG. The equations used are Coats-Redfern(CR) and Madusoodanan-Krishnan-Ninan(MKN) methods. The entropy of activation is negative for the first two stages showing that the compounds are more ordered in the activated state compared to the reactants. The positive value of ΔS for the third stage indicates irreversibility. The order of the reaction is 2.

Key words: Entropy of activation, Coats-Redfern equation, MKN method.

INTRODUCTION

Thermal analysis has been treated mainly as a chemical analysis tool till the middle of the century[1]. Depending upon the properties measured and the temperature program, [2-4] more than a dozen thermal methods are recognised. It is fairly common to complement all DTA data with TGA data[5]. 8-hydroxy quinoline and its derivatives are used as fungicides, amoebicides, bactericides and insecticides [6,7]. 8-hydroxy quinoline and its derivatives have found extensive application as analytical reagents in absorption spectrophotometry, fluorometery, solvent extraction and partition chromatography because of their ability to form complexes with many metal ions [8]. Phillips and O'Hara[9] determined the formula of the copper complex of oxine -5-sulfuric acid by the method of continuous variation. This paper deals with the thermal degradation studies and evaluation of kinetic parameters of the copper complex of oxine -5-sulphuric acid. Fig. -1 gives the structural formula of 8-hydroxyquinoline 5-sulphonic acid [8 (HQS)].

EXPERIMENTAL

8-hydroxy quinoline 5 sulphonic acid [8(HQS)] (Aldrich) were of analytical reagent grade. The other chemicals procured from Merck and were used as received. To Cu^{2+} solution was added dropwise 8-hydroxy quinoline-5-sulphonic acid with constant stirring. Above pH 5.0 turbidity appeared.

Then the solution was cooled and allowed to crystallise when the complex separated. The precipitate was dried in an air oven at 110^{0}C.

The solubility of the complex was tested in different solvents. Elemental analysis was done using a Pekin-Elmer 2400 series Analyser. The metal content was obtained by analytical methods[10]. Simultaneous TG A& DTG curves were recorded using Dupont 2100 thermal analyzer in conjunction with TGA thermo gravimetric analyser. The experiment was carried out in dry nitrogen atmosphere. The sample size was between 3mg and 10 mg and the heating rate was 10^0 or 20^0 min^{-1}. Magnetic susceptibility at room temperature was measured by Gouy method[11,12]. The scanning electron microscope (SEM) photographs were taken in a JEDL JSM 56000 LV SEM instrument.

The electronic spectrum was obtained from a Hitachi 320 uv-visible spectro photometer. For calculating the kinetic parameters Coats-Redfern[13] and Madusoodanan - Krishnan-Ninan[14](MKN) equations were used.

RESULTS AND DISCUSSION

Cu (II) 8 (HQS) is a crystalline solid soluble in water. Elemental and metal analysis shows that the metal ligand ratio is 1:2 and the complex contains

Table 1: Phenomenological data for the decomposition of [Cu (8HQS)$_2$. 2H$_2$O] complex

Stage of decomposition	Ti (K)	Tf (K)	Ts (K)	Weight loss
I	473	573	542.80	10.94
II	573	663	657.87	51.12
III	663	773	704.58	29.93

CR- parameter calculated as per CR equation; MKN –parameter calculated as per MKN equation

Table 2: Computational data for the first stage of the thermal decomposition of [Cu (8HQS)$_2$. 2H$_2$O] complex

T	I-T	α	CR	MKN
473	0.00211	-	-	-
483	0.00207	0.00756	-7.48589	-7.2752
493	0.00203	0.01925	-7.09278	-6.88139
503	0.00199	0.03713	-6.81699	-6.60492
513	0.00195	0.06669	-6.56617	-6.35343
523	0.00191	0.11757	-6.31237	-6.09897
533	0.00188	0.20077	-6.05343	-5.83938
543	0.00184	00.32453	-5.78795	-5.57326
553	0.00181	0.45173	-5.56956	-5.35426
563	0.00178	0.58856	-5.34553	-5.12962
573	0.00175	0.75564	-5.02603	-4.80951

CR- parameter calculated as per CR equation; MKN -parameter calculated as per MKN equation

two molecules of water of hydration. The composition of the complex from spectrophotometric studies confirm the metal ligand ratio as 1:2. The magnetic susceptilibility (μ_{eff}) is 1.84 BM. Scanning electron microscope (SEM) studies show that the reagent and complex are crystalline (Fig.-2a and Fig.-2b). The phenomenological data for the decomposition of $[Cu(8HQS)]_2.2H2O$)complex is given in Table -1.

The complex is stable upto 473 K. after which it starts decomposing. This decomposition ends at 573 K and the peak temperature is at 543 K and the weight loss is 10.94%. The second stage of decomposition starts immediately thereafter and approximately is over at 663 K. The third stage starts immediately thereafter and is completed at 773 K. In essence, all the three stages of decomposition follow one after the other without any stable

Table 3: Computational data for the first second stage of the thermal decomposition of [Cu $(8HQS)_2$. $2H_2O$] complex

T	I-T	α	CR	MKN
573	0.00175	-	-	-
583	0.00172	0.06749	-6.67483	-6.45772
593	0.00169	0.16080	-6.27151	-6.05382
603	0.00166	0.28110	-5.98348	-5.76522
613	0.00163	0.41412	-5.75067	-5.53186
623	0.00161	0.56240	-5.52031	-5.30094
633	0.00158	0.69973	-5.29689	-5.07698
643	0.00156	0.77739	-5.15285	-4.93241
653	0.00153	0.85837	-4.95586	-4.73489

CR- parameter calculated as per CR equation; MKN -parameter calculated as per MKN equation

Table 4: Computational data for the first third stage of the thermal decomposition of [Cu $(8HQS)_2$. $2H_2O$] complex

T	I-T	α	CR	MKN
663	0.00151	-	-	-
673	0.00149	0.06926	-6.78434	-6.56235
683	0.00146	0.16735	-6.73701	-6.15450
693	0.00144	0.31438	-5.02009	-5.5971
703	0.00142	0.54738	-5.61133	-5.38485
713	0.00140	0.81941	-5.04938	-4.82541
723	0.00138	0.90347	-4.74704	-4.52260
733	0.00136	0.95491	-4.40432	-4.17941
743	0.00135	0.98573	-3.84345	-3.61807
753	0.00133	0.99089	-3.71718	-3.49135
763	0.00131	0.99778	-3.11220	-2.88592

CR- parameter calculated as per CR equation; MKN -parameter calculated as per MKN equation

Table 5: Kinetic parameters for the thermal decompositionof [Cu (8HQS)$_2$. 2H$_2$O] complex

Stage of decomposition	Method	E (kJ mol-1)	A (S-1)	ΔS (JK-1 mol-1)	R	n
I	CR	134.8609	32.2 x 10^5	-125.32	0.9930	2.0
	MKN	135.0768	26.0 x 10^5	-127.10	0.9931	2.0
II	CR	173.531	27.6 x 10^5	-127.70	0.9940	1.8
	MKN	173.772	22.0 x 10^5	-110.45	0.9943	1.8
III	CR	396.203	1.89 x 10^{14}	20.79	0.0075	2.0
	MKN	396.305	1.419 x 10^{14}	18.39	0.9975	2.0

Table 6: T and (1-α) values for the thermal decomposition of [Cu (8HQS)$_2$ 2H$_2$O] complex [mass = 6.5557 mg; heating rate - 100C/min]

Stage	T (K)	(1-α)
I	473	-
	483	0.98999
	493	-
	503	0.97452
	523	0.95050
	533	0.84440
	543	0.73430
	553	0.57052
	563	0.40218
	573	0.22111
II	573	-
	583	0.99828
	593	0.99831
	603	0.99834
	613	0.99837
	623	0.99839
	633	0.99842
	643	0.99844
	653	0.99847
III	663	-
	673	0.93074
	683	0.83625
	693	0.68562
	703	0.45262
	713	0.18059
	723	0.04509
	743	0.01247
	753	0.00091
	763	0.000222
	773	

CR- parameter calculated as per CR equation; MKN - parameter calculated as per MKN equation

compounds in between. The total weight loss is 91.9%. The presence of water molecules is confirmed from TG analysis. According to Nikolaev *et.al*[15], water eliminated above 150^{0}C may be due to coordinated molecules.

The computed values for g ( ) / T^2 for the first stage of decomposition using the CR and MKN equations are shown in Table -2. This value is plotted against 1/T in Fig. -3. Similarly the computed data of g (α)/T^2 for the second and third stages are given in Tables 3 and 4 respectively. The plots of g (α)/T^2 against 1/T are shown in Fig.-4 and Fig.-5 respectively. The kinetic data is given in Table -5 and 1-α values are given in Table - 6.

The weight loss is higher than what can be accounted for by conversion to the respective oxide. It may be therefore summarised that the complex is volatile. The rate of decomposition is very fast and is lost by volatility. The DTA profile is given in Fig.-4. From the DTA profile, we observe that there are two small endothermic peaks, one at 270^{0}Cand another at 330^{0}C**.** These are due to the removal of molecules of water and partial decomposition of the complex. These endothermic peaks are followed by two exothermic peaks at 380^{0}C and 430^{0}C . The peak at 430^{0}C is the most prominent one. All the peaks have corresponding ones in the DTG curve(Fig.-6)

Regarding the kinetic parameters, the energy of activation in the first corresponds to 135 kJmol^{-1}. The second stage requires an energy of activation of around 175 kJ mol^{-1} and the third stage 396 kJ mol^{-1}. We understand that the entropy of

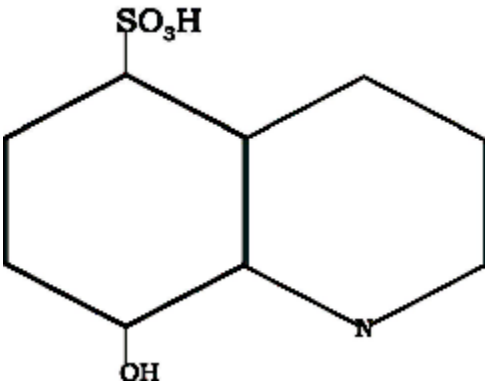

Fig. 1: Structural formula of the ligand

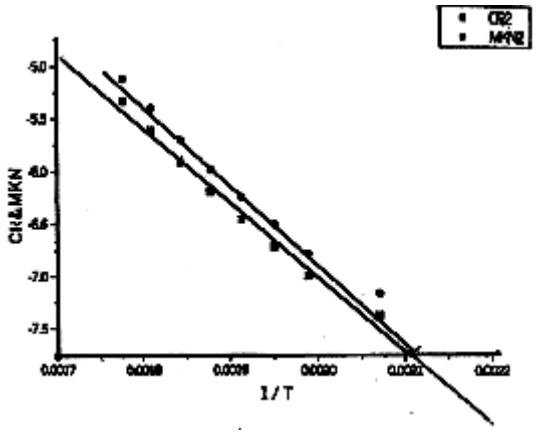

Fig. 3: Coats-Redfern and MKN plots for first stage of decomposition of [Cu (8HQS)$_2$, 2H$_2$O] complex

Fig. 2(a): Scanning electron microcrope (SEM) photograph of 8-HQS

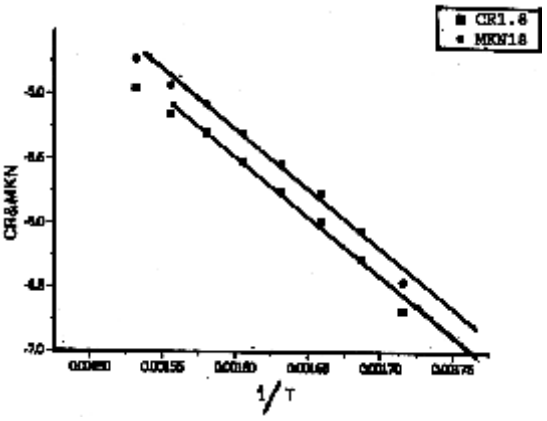

Fig. 4: Coats-Redfern and MKN plots for second stage of decomposition of [Cu (8HQS)2. 2H2O] complex

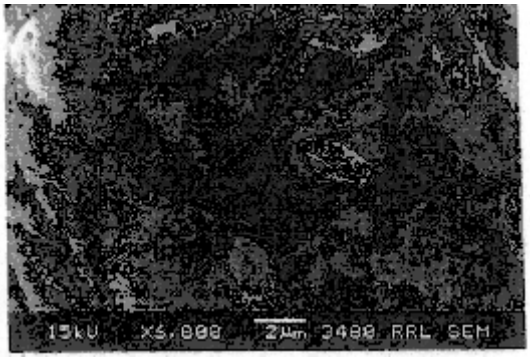

Fig. 2(b): Scanning electron microcrope (SEM) photograph of [Cu(8HQS)$_2$2H$_2$O complex

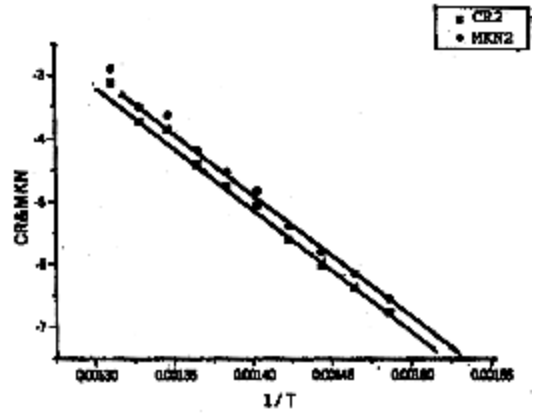

Fig. 5: Coats-Redfern and MKN plots for third stage of decomposition of [Cu (8HQS)$_2$. 2H$_2$O] complex

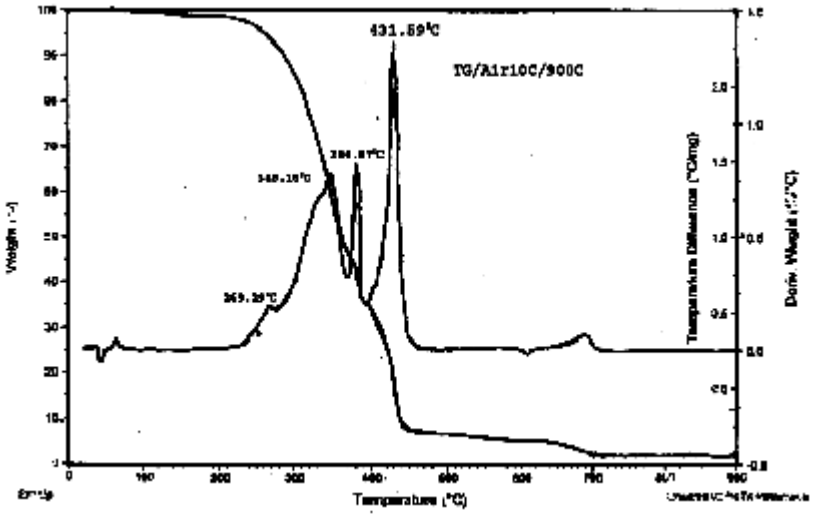

Fig. 6: Tg/DTG curve of [Cu(8HQS)$_2$2H$_2$O] Complex

activation is high especially at the third stage. The entropy of activation for the first two stages showing that at these steps, the compounds are more ordered in the activated stage compared to the reactants. The positive value of S for the third stage indicates irreversibility. The order of reaction is 2.

CONCLUSION

Copper(II) 8-hydroxy quinoline – 5 sulphuric acid is volatile. The compounds are more ordered in the activated state than in the reactants.

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