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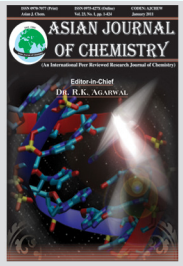

Kinetics of the Thermal Decomposition of Mn(II) Complex of 8-Hydroxyquinoline-5-sulphonic Acid

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Mn(II) 8-hydroxyquinoline-5-sulphonic acid complex has been prepared, identified and thermally analyzed. The kinetics of the thermal decomposition of the complex has been studied using thermogravimetry (TG) in conjunction with DTG and differential scanning calorimetry (DSC). The kinetic parameters such as energy of activation, pre-exponential factor, entropy of activation and order parameter have been calculated for well defined and decomposition of stage. The equations used are Coats-Redfern and Madusoodanan-Krishnan-Ninan methods. The correlation co-efficient are found to be closer to unity. DSC has been used to calculate the enthalpy changes involved in the removal of water of crystallizations at all stages of decomposition. The negative value for the entropy of activation for all the three stages show that the complexes are more ordered in the activated state than in the reactants. The DTA studies on the complexes corroborate with the DTG curves.

Key Words: Kinetics, Thermal decomposition, Mn(II), Complex, 8-Hydroxyquinoline-5-sulphonic acid.

INTRODUCTION

Thermal analysis is now established as an invaluable and rapid method for the characterization of materials and evaluation of kinetic and thermodynamic parameters over and wide range of temperature[1]. Prior investigators have reported thermal decomposition studies of manganese (II) complexes[2-4]. 8-Hydroxyquinoline and its derivatives are used as fungicides, amoebicides,bactericides and insecticides[5,6]. 8-Hydroxyquinoline and its derivatives have found extensive application as analytical reagents in absorption photometry, fluorometry, solvent extraction and in partition chromatography because of their ability to form complexes with many metal ions[7]. In the present studies, the kinetics and thermal properties of Mn(II) with 8-hydroxyquinoline-5-sulphonic acid (8-HQS) (Fig. 1) are described.

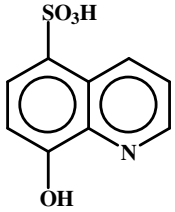

Fig. 1. Structural formula of the ligand

EXPERIMENTAL

8-Hydroxyquinoline-5-sulphonic acid (8-HQS) (Aldrich) were of analytical reagent grade. The purity of the ligand was checked by the Gran method[8]. The other chemicals procured from Merck and were used as received. To Mn(II) solution was added drop wise 8-hydroxyquinoline-5-sulphonic acid with constant stirring. The flesh coloured precipitate separated out was heated for 0.5 h with constant stirring. The precipitate was allowed to cool/filtered on a sintered crucible and washed with water several times. The crucible with precipitate was transferred to desiccator and allowed to dry to constant weight. Yield was 55 %.

The solubility of the complex was tested in different solvents. Elemental analysis was done using a Perkin-Elmer 2400 series analyzer. The metal content was obtained by analytical methods[9]. The electronic spectum was obtained from a Hitachi 320 UV-visible spectrophotometer. Scanning electron microscope (SEM) photographs were taken in a JEDL JSM 56000 LV SEM instrument. Simultaneous TG and DTG curves were recorded using Dupont 2100 thermal analyzer in conjunction with TGA, thermo gravimetric analyzer [Fig. 1(a)]. The experiment was carried out in dry nitrogen atmosphere. The sample size was between 3 and 10 mg and the heating rate was 10º or 20º min^{-1}. For calculating the kinetic parameters

Coats-Redfern (CR)[10] and Madusoodanan-Krishnan-Ninan (MKN)[11] equation were used.

RESULTS AND DISCUSSION

Mn(II) 8-hydroxyquinoline-5-sulphonic acid [Mn(II) 8-HQS] complex is a crystalline solid insoluble in acetone, benzene, carbon tetrachloride, chloroform, ethanol, *n*-hexane, *n*-heptane and methanol and water but soluble in ammonia and DMSO (dimethyl sulfoxide). Elemental and metal analysis show that the metal ligand ratio is 1:2 and the complex contains 2 molecules of water of hydration. The composition of the complex from spectrophotometric studies confirmed the metal to ligand ratio as 1:2. Fig. 2(a) gives the scanning electron microscope (SEM) photographs of the ligand (8-HQS) and Fig. 2(b) that of the complex $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$. SEM studies shows that the ligand and complex are crystalline.

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

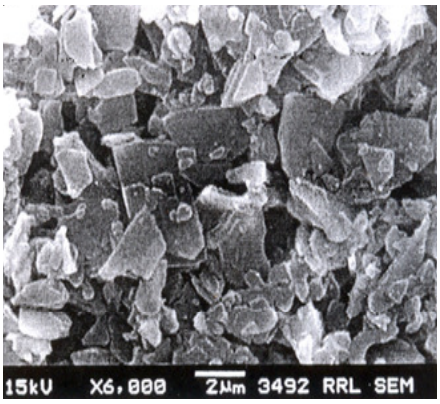

Fig. 2. (b) Scanning electron microcrope (SEM) photograph of $[Mn(8HQS)_2{\cdot}2H_2O]$ complex

The phenomenological data are given in Table-1. The complex $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ is stable upto 383 K as shown by the TG/DTG curve. First stage of decomposition occurs between 383-483 K. There is loss of 7.3 %. The peak temperature from the DTG curve is 434 K. The second stage decomposition occurs between 493-593 K and peak temperature is 555 K. The weight loss at the second stage comes to 11.9 %. The last stage of decomposition takes place between 653-793 K and weight loss of 52.6 %. The peak temperature of this third stage is seen at 745 K. The total weight loss corresponds to 71.8 % with 28.8 % as the resultant residue. The TG/DTG curve of the complex $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ is shown in Fig. 3.

TABLE-1
PHENOMENOLOGICAL DATA FOR THE DECOMPOSITION OF $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ COMPLEX

Stage of decomposition	T_i (K)	T_f (K)	T_s (K)	Weight loss (%)
I	383	483	434.05	7.30
II	493	593	555.14	11.87
III	653	793	745.93	52.56

T_i = Temperature of inception, T_f = temperature of completion; T = summit temperature.

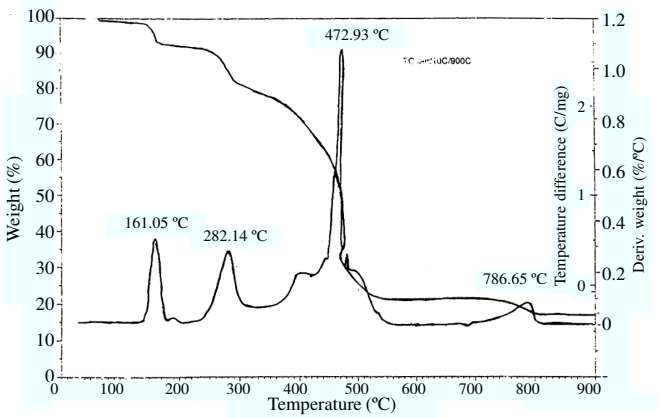

Fig. 3. TG/DTG curve of $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ complex

The computed values for $g(\alpha)/T^2$ for the first stage of decomposition using the CR and MKN equation are shown in Table-2. Similarly the computed data of $g(\alpha)/T^2$ for the second third stages are given in Tables 3 and 4, respectively. The T and $(1\text{-}\alpha)$ values are given in Table-5 and the kinetic data is given Table-6.

TABLE-2
COMPUTATIONAL DATA FOR THE FIRST STAGE OF THE THERMAL DECOMPOSITION OF $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ COMPLEX

T	1/T	α	CR	MKN
383	0.00261	0	6.63259	6.75166
393	0.00254	0.01683	-6.95532	-6.75166
403	0.00248	0.03647	-6.63259	-6.42808
413	0.00242	0.09257	-6.22326	-6.01791
423	0.00236	0.35905	-5.50436	-5.29819
433	0.00231	0.49509	-5.28150	-5.07454
443	0.00226	0.73773	-4.84366	-4.63592
453	0.00210	0.92146	-4.24282	-4.03432
463	0.00216	0.95652	-3.98744	-3.77949
473	0.00211	0.98738	-3.45639	-3.24642

CR-Parameter calculated as per CR equation; MNK-parameter calculated as per MKN equation.

TABLE-3
COMPUTATIONAL DATA FOR THE SECOND STAGE OF THE THERMAL DECOMPOSITION OF $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ COMPLEX

T	1/T	α	CR	MKN
493	0.00203	–	–	–
503	0.00199	0.01194	-7.32082	-7.10874
513	0.00195	0.02946	-6.93804	-6.72529
523	0.00191	0.09315	-6.42534	-6.21194
533	0.00188	0.14729	-6.21607	-6.00202
543	0.00184	0.29140	-5.85510	-5.64083
553	0.00181	0.49522	-5.49375	-5.27845
563	0.00178	0.71178	-5.10839	-4.89247
573	0.00175	0.82404	-4.84576	-4.62925
583	0.00172	0.88933	-4.62630	-4.40919
593	0.00169	0.94506	-4.31051	-4.09282

CR-Parameter calculated as per CR equation; MNK-parameter calculated as per MKN equation.

TABLE-4
COMPUTATIONAL DATA FOR THE THIRD STAGE OF THE THERMAL DECOMPOSITION OF $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ COMPLEX

T	1/T	α	CR	MKN
653	0.00153	–	–	–
663	0.00151	0.02593	-7.22304	-7.00155
673	0.00149	0.06068	-6.85810	-6.63610
683	0.00146	0.09807	-6.65286	-6.43036
693	0.00144	0.13413	-6.51989	-6.29690
703	0.00142	0.16983	-6.42006	-6.19658
713	0.00140	0.21060	-6.32725	-6.10328
723	0.00138	0.25700	-6.23897	-6.01453
733	0.00136	0.34116	-6.10069	-5.87578
743	0.00135	0.46665	-5.92989	-5.70452
753	0.00133	0.85102	-5.43993	-5.20610
763	0.00131	0.89066	-5.37106	-5.14478
773	0.00129	0.92899	-5.29525	-5.06853
783	0.00128	0.96335	-5.19354	-4.96638
793	0.00126	0.98741	-5.05910	-4.83150

TABLE- 5
T AND (1-α) VALUES FOR THE DECOMPOSITION OF $[Mn(8\text{-}HQS)_2{\cdot}2H_2O]$ COMPLEX [MASS = 8.5811 mg; HEATING RATE = 10 ºC/min]

Stage	T (K)	(1-α)
I	383	–
	393	0.98319
	403	0.96353
	413	0.90743
	423	0.64095
	433	0.50491
	443	0.26227
	453	0.78540
	463	0.43480
	483	0.01262
II	493	–
	503	0.98806
	513	0.97054
	523	0.90685
	533	0.85271
	543	0.70860
	553	0.50478
	563	0.28822
	573	0.17596
	583	0.11067
	593	0.05494
III	653	–
	663	0.97407
	673	0.93932
	683	0.90193
	693	0.86587
	703	0.83017
	713	0.78940
	723	0.78940
	733	0.74300
	743	0.65884
	753	0.14898
	763	0.16934
	773	0.07101
	783	0.03645
	793	0.42590

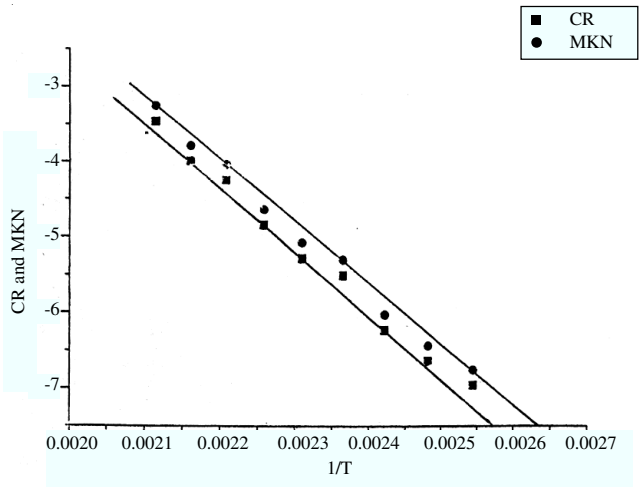

Fig. 4. Coats-Redfern and MKN plots for first stage of decomposition of complex [CR = log $\{(1 - \alpha)^{1-n})/(1 - n)\}/T^2$ and MKN = log $\{(1 - \alpha)^{1-n}/(1 - n)\}/T^{1.9215}$]

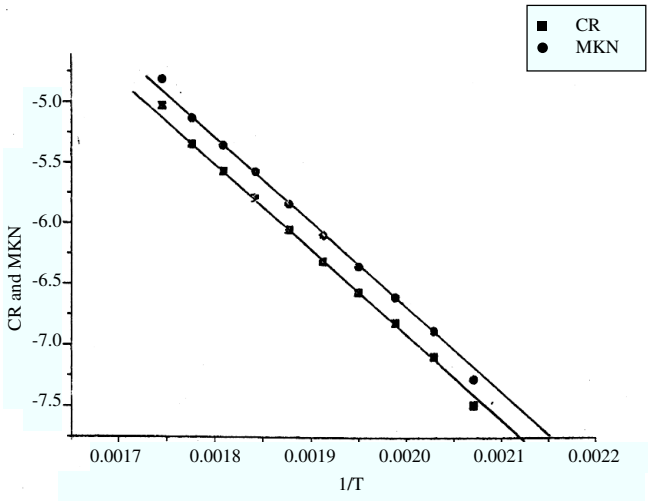

Fig. 5. Coats-Redfern and MKN plots for second stage of decomposition of $[Mn(8HQS)_2{\cdot}2H_2O$ complex

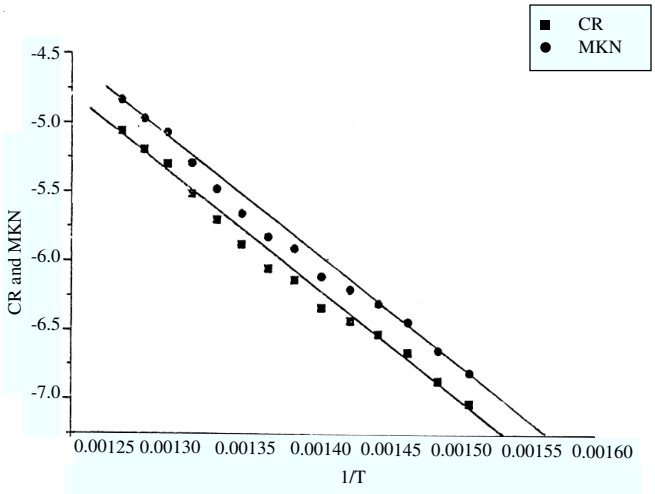

Fig. 6. Coats-Redfern and MKN plots for third stage of decomposition of $[Mn(8HQS)_2{\cdot}2H_2O$ complex

The result of the kinetic studies of the complex is based on the integral methods of Coats and Redfern (CR) and that of MKN. Figs. 4-6 give the Coats-Redfern and MKN plots for the first, second and third stage decomposition of $[Mn(8HQS)_2{\cdot}2H_2O]$ of complex. The values for the energy of activation by the CR equation or 157.43, 190.40 and 161.51 corresponding to 157.56 and 161.83 kJ mol^{-1} by the MKN equation. Both the values are very close to each other. The pre exponential factors

TABLE-6
KINETIC PARAMETERS FOR THE THERMAL DECOMPOSITION OF $[Mn(8\text{-}HQS)_2 \cdot 2H_2O]$ COMPLEX

Stage of decomposition	Method	E (kJ mol^{-1})	A (s^{-1})	DS (JK^{-1} mol^{-1})	R	n
I	CR	157.432	3.160×10^9	-66.19	0.9957	2.0
	MKN	157.568	2.990×10^9	-68.49	0.9958	2.0
II	CR	190.405	1.004×10^9	-77.77	0.9986	2.0
	MKN	190.585	7.900×10^9	-79.76	0.9986	2.0
II	CR	161.510	8.500×10^5	-138.99	0.9860	1.1
	MKN	161.834	7.100×10^5	-140.50	0.9861	1.1

are high and are indicative of the entropy of activation. The negative values for the entropy of activation for all the three stages show that the complexes are more ordered in the activated state than in the reactants. The order of reaction is 2 for the first 2 stages and 1 for the third stage. Similar results have been reported earlier for Mn(II) complex with other ligands[12].

From the TG/DTG curve of Mn-8 HQS complex (Fig. 3), it is seen that there are two endothermic peaks, one at 160 ºC and another at 280 ºC. These peaks are rather small. There is a prominent exothermic peak at 470 ºC. All these three peaks are corroborated by DTG profile. The endothermic peaks can be ascribed to the removal of water and possibly the initial decomposition. The endothermic peak is due to oxidation of the organic residue left on removal of the molecule of water. From the DSC profile it is seen that there are two major enthalpy changes, one at 225 ºC and another at 317 ºC. Using the software PEAK, the transition enthalpy changes have been calculated. For Mn(8-HQS) complex the enthalpy change is 322 J/g.

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