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Research Paper

Kinetic Study of the Oxidation of Glyoxylic Acid (Hgl) by Mniii Complex of (H2 Salen=N,Ni-Bis(Salicylidene)Ethane-1,2-Diamine.

Engineering

KEYWORDS : Glyoxylic acid, salen ligand, kinetic study

Priyambada Jena | College of engineering and technology,Bhubaneswar

ABSTRACT

The kinetics of oxidation of glyoxylic acid (HGl) by MnIII(salen)(OH2)+2 ((H2salen =N,N'-bis(salicylidene) ethane-1,2-diamine) is investigated at 25.0–35.0◦C, 1.76≤pH ≤5.20, I =0.3 mol dm–3(NaClO4). The products are identified as formic acid, CO2 and Mn(II) with the reaction stoichiometry. The overall reaction involves fast equilibrium pre-association of Mn(III)(salen)(OH2)+2 with HGl and its conjugate base Gl– forming the corresponding inner sphere complexes (both HGl and Gl–being the monohydrate gem-diol forms) followed by the slow electron transfer steps. The rate, equilibrium constants and activation parameters for various steps are presented.MnIII(salen)(OH2)(Gl) is virtually inert to intra molecular electron transfer while the process is facile for MnIII(salen)(OH2)(HGl)+ reflecting the involvement of proton coupled electron transfer mechanism .
MnIII(salen)(OH2)(HGl)/Gl)+/0+HGl/Gl– →products, shows that HGl for the (aqua)(HGl) complex is a better reducing agent than Gl–.

1.INTRODUCTION:-

Manganese is the third most abundant transition metal in earth's crust and can exist in different formal oxidation states ranging from –I to +VII. The high reduction potentials of +3 and +4 oxidation states of Mn cycle in aquatic environments are linked to a significant degree, with geochemical cycles of carbon, oxygen, iron, sulphur, arsenic and other redox elements. Studies on high valent manganese complexes irrespective of their nuclearity, are of high importance because of their potential uses in various biological as well as non-biological redox processes [1-3] and in photosynthesis. Since manganese in its +3 oxidation state is involved in most of the processes, the kinetics and mechanistic studies of the redox reactions of Mn (iii) complexes are important in ligand substitution and electron transfer reactions as well as in biomimetic chemistry. A review of the redox reactions of mononuclear Mn(iii) complexes, essentially of aminopolycarboxylate ligands, appeared several years ago which describes briefly the mechanism which aspects of such reactions[4-5]. Recently a novel binuclear MnIII complex, [MnIII 2, III (tpdm) 2(μ-O) (μ-OAc2)] 2+ (tmpd = tris (2-pyridyl) methane) has been modelled as Nature's water oxidation catalyst [6]. However, there is little success in this regard. The redox sensitivity of this metal ion in higher oxidation states has been exploited in several synthetic and limited kinetics studies in the past [7]. In continuation of our current interest on the redox reactions of Mn(iii)L [8,9],we have chosen glyoxylic acid ,HGl as the reductant due to its importance in metabolic processes and plant physiology[10-11]. However every new complexes formed by Mn in +III/IV state offers challenges in respect of understanding the mechanistic aspects of reactions with reducing/ oxidizing agents as rates and paths of reactions are likely to be characteristic features of the reacting partners[7]. Also the idea using HGl as one of the reactant has come from recent studies [12-15], where it was reported that organic acid and oxo-carboxylic acids were found to be secondary organic aerosols (SOA). In that context, we report here a detailed study of the kinetics and mechanism of the oxidation of glyoxylic acid by Mn(salen) complex, under varying p^H conditions and temperature and to develop a kinetic model for the Mn(iii)L-HGl system.

2. EXPERIMENTAL

2.1:- MATERIALS AND REAGENTS.

MnIII(salen)Cl,H2O was prepared by the published method essentially as described by Sharpe and co-workers [16]. The elemental analysis was in satisfactory agreement with UV-Vis, IR spectra [17]. For MnIII(salen)(OH2) + 2 (generated in situ, pH 4, aqueous medium) λmax, nm (ε, dm3 mol–1 cm–1):235(40,241), 279(18,115) which agreed well with previously reported values [18]. Glyoxylic acid monohydrate, HGl (AR, Sigma Aldrich, purity 98%), MeOH (G.R. Merck 99.8%) and acetic acid (AR,Qualigens) were used as received. The concentration of glyoxylic acid was further checked by potentiometric titration using standard NaOH. All other chemicals were of highest purity available. The water was doubly distilled, the second distillation being made from alkaline KMnO4 in all glass (borosil) distillation apparatus. Freshly distilled water was used to prepare solutions for kinetic runs. The stock solution of the complex (2 × 10 –3 mol dm–3) was protected from light and stored in a refrigerator. Ionic strength (I) adjustment was done with NaClO4 which was prepared by mixing freshly prepared and standardised stock solutions of NaOH and HClO4. The p^H of the stock solution was adjusted to 5.5-6.0 and the concentration checked by a combined ion exchange alkalimetric procedure using Dowex 50W X8 resin in the H+ form [19].

2.2:- PHYSICAL MEASUREMENTS.

A Systronics (India) model 118, and a Perkin Elmer Lambda 25 UV-visible spectrophotometers with a matched pair 10 mm quartz cells were used for all absorbance measurements. The I R measurements were made on a Perkin Elmer FTIR spectrometer, model Spectrum 2 using KBr pelletS. ESR measurement was performed on a JEOL (Japan) JES-FA 200 ESR spectrometer at room temperature operating in Xband mode (8.75–9.65 GHz, power 1.08 W, sensitivity 7 × 109 spins/0.1 mT, and resolution 2.35 μT). The pH measurements were made with a Systronics (India) pH meter model 335 using a glass-Ag/AgCl, Cl– (3 mol dm–3 NaCl) electrode CL 51. NBS buffers of pH 4.01, 7.01 and 9.20 prepared from KHphthalate, Na2HPO4/ NaH2PO4, and Na2B4O7, 10H2O, respectively were used to calibrate the pH meter. The measured pH of the reaction medium was converted to p[H+] (= -log[H+]) by the relationship p[H+] = (1.09 ± 0.02)pH - 0.318 ± 0.075 established by a calibration curve using dilute HClO4 solutions (1.98 × 10–2 ≤ [H+] / mol dm–3 ≤ 1.00 × 10–5) at the same ionic strength as mentioned in the reaction media (I=0.3 mol dm–3) [20].

2.3:- KINETICS.

The kinetics of the reaction between the complex, MnIII(salen)(OH2)Cl, instantaneously aquates10 to [MnIII(salen)(OH2)2] + and HGl was monitored spectrophotometrically under pseudo first order condition at 25.0 ≤ t, ◦C ≤ 35.0. The reaction mixture containing all components except the complex was equilibrated in 50 cm3 measuring flask in a water thermostat maintained at the desired temperature (±0.1◦C). After thermal equilibrium was reached, 1cm3 of the complex was quickly transferred into the reaction mixture and made up to the volume. The concentration of complex [MnIII(salen)(OH2)2] + was varied as (3–4) × 10–5 and that of [Gl]T (= total glyoxylic acid concentration) in the range of 0.005–0.05 mol dm–3. The ionic strength of the medium was fixed at 0.3 mol dm–3 (NaClO4) unless otherwise quoted. The pH of the reaction mixture varied in the range of 1.76–5.20 by self-buffering due to glyoxylic acid/glyoxylate which could be

achieved by addition of standard solution of NaOH/HClO4 to glyoxylic acid solution. Rate measurements were done at 280nm.

The observed rate constants (kobs) were calculated by fitting the absorbance (At) – time (t) data to equation (1)

$A_t = (A_0 - A_\infty) \exp(-k_{obs}t) + A_\infty$ ----------(1)

A_∞ was close to zero for the completion of the reaction. The initial absorbance was in the range of 0.5-0.7. For very slow reaction ($k_{obs} \sim 10–5–10–6$ s–1) the rate constants were evaluated by the method of initial rate, fitted to equation (2), a limiting form of equation (1).

$A_t = C'\exp(-k_{obs}t) = C' - C'.k_{obs}t.$ ---------- (2)

Where $c' = A_0[1-(A_\infty/A_0)]/1-(A_\infty/A_t)]$

The observed rate data are presented in tables (1,2and 3)

Table 1. (Rate data for the reduction of $Mn^{III}(salen)(OH_2)_2^+$ by Glyoxalate (Gly) at 25.0◦C.[a])

$[HGl]_T$/ mol. dm^{-3}	pH[a]	$10^5k_{obs}/s^{-1}$	$10^5k_{cal}/s^{-1}$
0.005	2.31	0.185	0.21
0.007	2.26	0.22	0.28
0.009	2.24	0.38	0.36
0.015	2.20	0.49	0.72
0.020	2.16	0.99	1.07
0.035	2.10	1.78	1.81
0.040	2.05	2.82	2.65
0.050	1.98	3.38	3.57
0.030	2.98	0.45	0.38
0.030	3.15	0.32	0.41
0.030	3.89	0.24	0.24
0.030	4.18	0.17	0.21
0.030	5.13	0.12	0.15

Table 2. (Rate data for the reduction of $Mn^{III}(salen)(OH_2)_2^+$ by Glyoxalate (Gly) at 30.0◦C.[a])

$[HGl]_T$/ mol. dm^{-3}	pH[a]	$10^5k_{obs}/s^{-1}$	$10^5k_{cal}/s^{-1}$
0.005	2.35	0.26	0.21
0.007	2.28	0.38	0.32
0.009	2.23	0.54	0.44
0.015	2.18	0.76	0.72
0.020	2.14	1.12	1.09
0.035	2.08	1.99	1.95
0.040	2.02	2.82	2.82
0.050	1.97	3.56	3.57
0.030	3.01	0.58	0.53
0.030	3.13	0.45	0.45
0.030	3.87	0.28	0.31
0.030	4.20	0.22	0.22
0.030	5.11	0.18	0.20

Table 3. (Rate data for the reduction of $Mn^{III}(salen)(OH_2)_2^+$ by Glyoxalate (Gly) at 35.0◦C.[a])

$[HGl]_T$/ mol. dm^{-3}	pH[a]	$10^5k_{obs}/s^{-1}$	$10^5k_{cal}/s^{-1}$
0.005	2.37	0.48	0.45
0.007	2.28	0.77	0.79
0.009	2.25	0.83	0.85
0.015	2.19	1.03	1.06
0.020	2.14	1.27	1.26
0.035	2.09	2.15	2.17
0.040	2.01	3.03	3.01
0.050	1.98	3.87	3.83
0.030	2.99	0.65	0.65
0.030	3.12	0.54	0.62
0.030	3.87	0.38	0.35
0.030	4.18	0.27	0.27
0.030	5.12	0.21	0.19

2.4:- PRODUCT ANALYSIS AND STOICHIOMETRY.

The reaction mixture containing Mn(III)(salen) + excess HGl at different pHs were allowed to stand at 30◦C for completion reaction. The brown colour of the complex was fully discharged (10t1/2) indicating complete reduction of Mn (III). The unreacted HGl was then estimated by the method of Kramer etal [21] which involved the formation of a pink coloured formazan derivative of HGl using phenyl hydrazine and $K_3Fe(CN)_6$ and measuring absorbance at 520 nm. The details of the procedure adopted has been described by Nayak and co-workers [22]. We obtained,– $\Delta[HGL]/ - \Delta[Mn^{III}(salen)] = 1.99\pm0.05$, indicated that the average consumption of Mn(III) per mol of HGl. The product manganese species was Mn (II) (IN=5/2) as evidenced from the 6 line ESR spectrum of the spent reaction mixture (see figure1) .The other products of the oxidation are formic acid and CO_2.

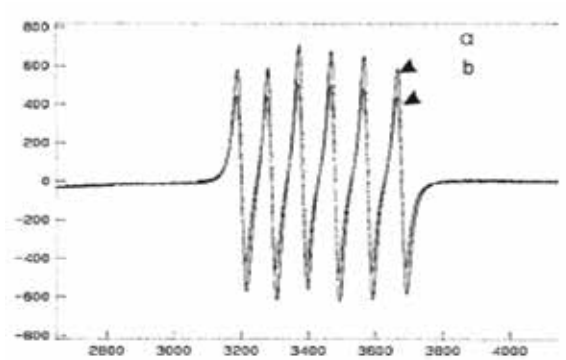

Figure-1. (Six line ESR spectrum of the product manganese (II) in solution of $Mn^{III}(salen)(OH_2)_2^+$ + HGl after completion of the reaction.)

2.5:- TEST FOR FREE RADICAL.

The reaction carried out at p^H=2.5(adjusted with HClO4) with $[HGl]_T$=0.04, $[Mn^{III}(salen)]_T = 3.05X10^{-5}$,I=0.3 mol dm^{-3} , 35◦C in the presence of [acrylamide]T =0.01-0.04 yielded $10^5k_{obs}/s^{-1}$ as 2.01,1.75,1.42,1.23. This small decreasing trend of kobs distinctly shows the involvement of a radical intermediate from glyoxylic acid which reacted with Mn(III)(salen)

Instantaneously to maintain the stoichiometry as shown in equation (3) but was scavenged by acrylamide causing a decrease in the overall rate constant (kobs).

$2Mn(III)(salen)(OH2)^+_2 + CH(OH)_2CO_2H = 2MnII(salen)(OH_2)_2 + HCO_2H + CO_2 + 2H^+$ ---------- (3)

2.6:- DETECTION OF OXIDATION PRODUCTS.

Under the conditions ($1.9 \le p^H \le 5.20$), CO2 and formic acid were the oxidation products of glyoxylic acid. CO2 was detected qualitatively by GC analysis [23] and formic acid by the chromotropic acid test [24-26]. It may be noted that glyoxylic acid containing a formyl group which developed a red coloration in the chromotropic acid test.

3.RESULTS AND DISCUSSION.

3.1:- PRELIMINARY OBSERVATIONS

The repetative scans of the reaction mixture ($200 \le \lambda$, nm≤ 700) at pH =2.48 over extended time displays a steady decrease of absorbance at all wavelengths with an isobastic point at 26 nm. Again TH EREDUCTION OF Mn(iii) to Mn(ii) was evident as the deep brown color of the reaction mixture of Mn(iii)(salen) complex and HGl became colorless. Hence the spectral behaviour is in conformity with the reduction of Mn(iii) by glyoxylic acid.

3.2:- EQULIBRIA OF GLYOXYLIC ACID.

The fast hydration/dehydration equilibria of glyoxylic acid and its conjugate base in water has been wellstudied and discussed at length by Nayaket al [27].The acid and its anion exist in the monohydrate form (gemdiol) to the extent of>99% and 93–95%, respectively.We, therefore, consider the protolytic equilibrium of HGl in terms of the gem-diols.

3.3:- EFFECT OF IONIC STRENGTH.

The reaction is relatively complex, that it involves several rate and equilibrium steps. At constant p^H (2.28), $[HGl]_T$=0.030 mol. dm^{-3} (30◦C and 0.01≤I/mol.dm^{-3}≤0.4. Under this condition >88% of $[HGl]_T$ exist and a small rate retardation of the overall rate with increase of ionic strength.

4.ANALYSIS OF RESULTS.

From the experimental datas ,the reaction of HGl with Mn(iii)(salen)$(OH_2)_2^+$ was redox reaction succeeding the initial fast equilibrium complexation of Mn(iii)(salen) by HGl/Gl^-. The pseudo-first order rate constant at varying $[HGl]_T$, p^H (1.75-5.20) and temperatures (25.0-35.0◦C) in tables 1,2 and 3. A clear evidence for the greater than first order dependence of k_{OBS} on $[HGl]_T$ emerges(at constant p^H 2.15 at 30◦C). Similar trend was observed at other temperatures. Here the major reductant species is HGl. However k_{OBS} at constant $[HGl]_T$(0.03,M) reflects steadily decreasing trend with increase of p^H at all temperatures. This indicates that Gl^- ,in contrast to our expectation is not a superior reducing agent (kinetically) than its conjugate acid,HGl.

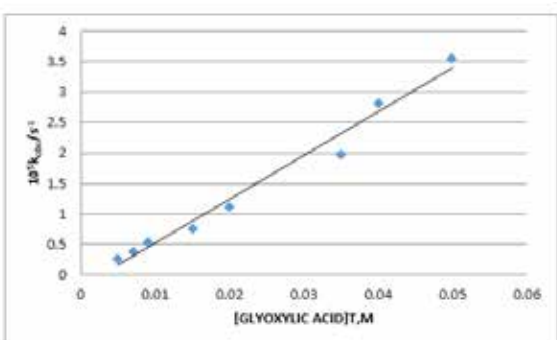

Figure.2 (10^5 K_{obs}/s^{-1} VS [GLYOXYLIC ACID]T,M plot at 30^0C)

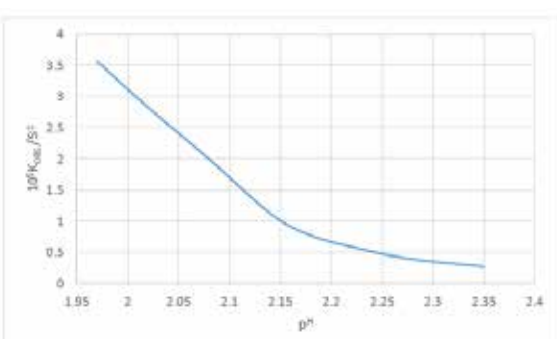

Figure.3 (10^5 K_{obs}/s^{-1} VS p^H [GLYOXYLIC ACID]T= 0.03M, 30^0C)

Our results indicate that internal electron transfer from the coordinated glyoxylate to Mn(III) In Mn(III)(salen)(OH2)(Gl) is not a favourable process as compared to the same for its conjugate acid analogue, MnIII(salen)(H2O)(HGl)+. The redox activity is inversely related to the thermodynamic stability. The nature of the two complexes can be judged considering the outer-sphere association of Gl– and HGl with Mn(III)(salen)(OH2)+2 on statistical considerations and theory of diffusion[30,31].

Notable fact is that there is no hydrogen bonding of the OH groups of the gem-diol moiety and Gl– acts as a mono dentate ligand for the metal centre. Contrastingly, the HGl moiety binds Mn(III)(salen) virtually as a bi-dentate ligand, with one bond to Mn(III) via the–C=O function and the other via a hydrogen bond involving the carboxyl proton and the bound phenoxide. However, our computational strategy attempts to differentiate the mechanistic path ways of reduction of Mn(III)(salen)(OH2)(Gl) by Gl– and Mn(III)(salen)(H2O)(HGL)+ by HGL; the former involves inner sphere mechanism unlike the latter for which the outer sphere mechanism. A comparison of the second order rate constants also reveals that HGl reduces much faster than Gl– unlike in several other cases where reverse sequence has been reported for anions and their conjugate acids reducing various Mn(III) complexes[32].

5. CONCLUSION.

The electron transfer reaction between glyoxylic acid and Mn(III)(salen)(OH2)+2 involves equilibrium pre-association of the reactants yielding innersphere complexes, Mn(III)(salen)(OH2)(Gl) and MnIII(salen)(OH2)(HGl)+, where HGl and Gl– are the gem-diols of the acid and the conjugate base forms of the reductant, respectively. Computational study shows that the proton of the carboxylic acid function is hydrogen bonded to one of the coordinated phenoxide function while both the diol-OH groups are not involvedin H-bonding in the state of coordination of HGl and Gl– to Mn(III). There is remarkable kinetic stability of MnIII(salen)(H2O)(Gl) towards intra-molecular electron transfer in contrast to moderate rate of intra-molecular reduction of Mn(III) centre by the coordinated HGl. This electro-protic reaction through the influence of H-bond, is considered to be a clear case of 'proton coupled intra-molecular electron transfer' process.

However,MnIII (salen)(H2O)(Gl) further undergoes reduction of Mn(III) centre by Gl– in a second order process as also Mn(III)(salen)(H2O)(HGl)+ by HGl; computational study, however, indicates the possibility of adduct formation between MnIII(salen)(OH2)(Gl) and Gl– But not between MnIII(salen)(OH2)(HGl)+ and HGl. We conclude that the intimate reduction steps follow innersphere mechanism possibly except in the second order path of the reaction between MnIII(salen)(OH2)(HGl) and HGl.

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