Kinetics of Oxidative Degradation of Oxalatopentammine Cobalt (III) Perchlorate by Aqueous Colloidal Manganese Dioxide

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Abstract- Kinetics of the oxidative degradation of Oxalatopentammine Cobalt (III) perchlorate complex by colloidal MnO_2 in acid medium has been studied by varying concentration of the complex from 2.8×10^{-4} to 4.8×10^{-3} mol dm^{-3} ,colloidal MnO_2 from 1.6×10^{-5} to 2.6×10^{-5} mol dm^{-3} and $HClO_4$ concentration from 1.0×10^{-4} to 1.0×10^{-3} moldm^{-3} using UV-Visible spectrophotometer at the wave length of 375nm. Pseudo-first-order conditions are maintained in each kinetic run. It has been found that the values of rate constants remained constant for all concentrations of colloidal MnO_2. So the reaction is pseudo 1st order with respect to colloidal MnO_2. A plot of log k versus log $[HClO_4]$ is linear with a slope of 0.5742 which confirmed that the reaction is less than first order with respect to $[HClO_4]$. A plot of log k versus log [complex] is linear with a slope of 1.30741 which confirmed that the reaction is first order with respect to the complex.

Key words: Colloidal MnO_2, kinetics, oxidative degradation

I. INTRODUCTION

Manganese dioxide has been most extensively studied due to its good oxidizing property [1-4] and reasonably high catalytic activity [5-8]. It is one of the most extensively used heterogeneous catalysts for a variety of organic and inorganic transformations in gaseous as well as liquid phases. However, its use in homogeneous catalysis is limited because of its insolubility under ordinary reaction conditions. In order to remove this limitation, the idea of preparation of colloidal MnO_2 came to the mind of different researchers across the globe. As the colloidal manganese dioxide is water-soluble, it can be used as a homogeneous catalyst for many reactions.

The synthesis of several forms of stable and perfectly transparent colloidal MnO_2, either in aqueous [9,10] or organic media has made the kinetic study of its oxidizing behavior in redox reaction possible by conventional UV-visible spectrophotometeric method [11]. Keeping these in view, the kinetics and mechanism of oxidation of simple organic molecules like oxalic acid, lactic acid, D-fructose etc by colloidal MnO_2 have been studied [12-19]. Benito and his co-workers at University of Barcelona, Spain have extensively studied the synthetic parameters (like coagulation and stabilization) and catalytic properties of colloidal manganese dioxide. The coagulation of colloidal MnO_2 by divalent metal cation, oxidation of Mn(II), formic acid and oxalic acid etc have been reported [12,14,20,21]. Photo induced reaction between colloidal MnO_2 and some organic compounds of environmental importance have been reported [22]. It is known that carboxylic acid (oxalic acid, malonic acid etc.) and amino acid (glycine, alanine, iminodiacetic acid, pyridine-2/3- carboxylic acid etc.) are bound to a variety of metal ions in biological and chemical systems. The rate and mechanism of oxidation of these bound ligands is different from those of free ligands. A detailed kinetic study is needed to assess the oxidizing ability of colloidal MnO_2 towards these coordinated ligands and also to predict the most probable mechanism. This would add further input on its application in reaction of chemical and biological importance.

The present work deals with the study of the catalytic activity of colloidal Manganese dioxide for the oxidation of Oxalatopent ammine Cobalt (III) perchlorate complex.

II. EXPERIMENTAL

2.1. Preparation of the Complex

An aqueous solution containing 1.4 g of oxalic acid was added to a solution of aqua pentamminecobalt (III) per chlorate (prepared by dissolving 4.6 g of aqua complex in 30ml of water) and heated at $60-70^0$c for about four hours. The resultant solution was cooled in an ice bath and the oxalato complex was precipitated by adding drop wise 70 percent perchloric acid. The contents were allowed to stand in an ice bath for about 20 minutes to ensure complete precipitation. The compound was then filtered, washed with several portions of absolute alcohol and then with ether.

The crude complex was dissolved in minium volume of hot water and then filtered. The filtrate was cooled in an ice bath and few drops of 70 percent perchloric acid was then added, when the oxalato complex precipitated out. The crystals were filtered, washed thrice with ethanol

and then thrice with ether. Two to three such crystallizations were necessary to obtain a compound which was sufficiently pure for kinetic measurement.

2.2. Characterisation of the complex

2.2.1. Elemental analysis

The purity of the complex was checked by elemental analyses. The metallic component in the complex was estimated by standard wet chemical analysis.

2.2.2 Spectral study

The UV- visible spectral measurements of the prepared complex were made using Shimadzu UV-2450 and Systronics 119 double beam UV-visible spectrophotometers. Infrared spectra in KBr phase were recorded using Shimadzu IR-Affinity-1 FT-IR spectrophotometer . The spectra were recorded at a resolution 4 cm^{-1} and averaging 32-64 scans in the range of 4000-400cm^{-1}.

2.3. Chemicals used

Analytical grade reagents were used for preparation of all standard solutions. For synthesis of complexes and colloidal MnO_2, analytical grade chemicals were also used as far as practicable. All solutions were prepared in doubly distilled water.

2.4. Preparation of Colloidal MnO_2

A dark-brown Colloidal MnO_2 (5.0 x 10^{-4}M) Solution was prepared by reducing $KMnO_4$ with a stoichiometric amount of $Na_2S_2O_3$ according to the reaction,

$$8\ MnO_4 + 3S_2O_3^{2-} + 2\ H^+ \longrightarrow 8\ MnO_2 + 6\ SO_4^{2-} + H_2O$$
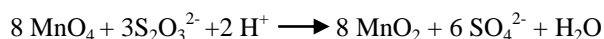
A 2L volumetric flask was filled with water to around 4/5 of its capacity. 20ml of $Na_2S_2O_3$ (1.88 x 10^{-2}M) solution was added to it. Then 2ml of $KMnO_4$ (0.2M) Solution was added & the mixture was diluted to 2-L with more water. Each addition was followed of homogenization by gentle shaking. A dark brown coloured colloidal solution was obtained, remaining perfectly transparent at least for several months.

2.5. Characterization of Colloidal MnO_2

The colloidal solution so prepared ([MnO_2] = 5 x10^{-4}) was characterization by means of Malvern autotimer 2.C, the results indicating that that 90% of the colloidal particles had a diameter comprised in the range 89-193 nm with a peak at 120nm.. The zeta potential (measured with a Malvern zeta-sizer 4.C) was – 47 + 3mV. Coagulation experiments indicated that the colloidal particles had a negative electrostatic charge, thus indicating that their stability in solution was probably due to the fixation of some anions on the colloidal surface. The colloid's UV-Vis spectrum was recorded with Shimadzu UV-2450 and Systronics 119 double beam UV-visible spectrophotometers and showed a large band covering the whole visible region of the spectrum, with absorbance uniformly decreasing with increasing wave length, as well as a wide maximum at 300-400 nm.

2.6. Kinetics of Spectrophotometric measurement

The reaction was initiated by adding the required quantity of colloidal MnO_2 maintained at constant temperature to the mixed solution of HCO_4 and the complex maintained at the same temperature. The zero time was taken when half of the colloidal MnO_2 solution was added. The rate of disappearance of MnO_2 was monitored at 375 nm at different time intervals with a UV-Visible Spectrophotometer, using a cell of path length 1cm. The pseudo-first order rate constants were calculated from the slopes of plots of log (absorbance) versus time. The first-order plots in almost all cases were linear to 80% completion of the reaction with correlation coefficient ~0.998.

III. RESULTS AND DISCUSSION

3.1 Characterization of colloidal MnO_2

The colloid's UV-Vis spectrum was recorded with a Shimadzu UV-2450 spectrophotometer, and showed a large band covering the whole visible region of the spectrum, with absorbance maxima at 375 nm (Fig1). So the wavelength of 375nm was chosen to follow the kinetic runs.
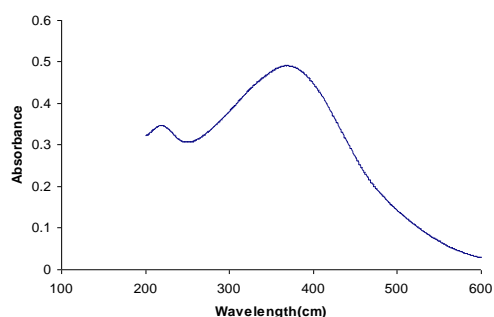

Fig.1.   UV-Visible Spectra of Colloidal MnO_2

3.2 Characterization of the complex UV-Vis Spectra:-

The UV-Vis spectrum of the complex was recorded with a Shimadzu UV-2450 spectrophotometer, and showed a large band covering the whole visible region of the spectrum, with absorbance maxima at 500 nm (Fig2).
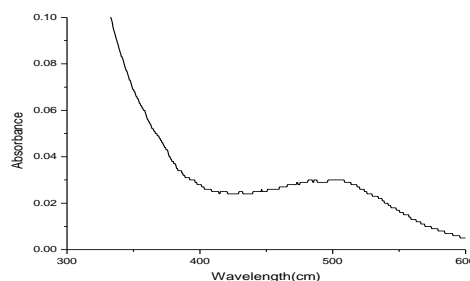

Fig:2 UV-Visible Spectra of Oxalato pentammine Cobalt (III) perchlorate complex

IR Spectra:-

Infrared spectra in KBr phase were recorded using Shimadzu IR-Affinity-1 FT-IR spectrophotometer available at our Department. The spectra were recorded

at a resolution 4 cm^{-1} and averaging 32-64 scans in the range of 4000-400cm^{-1}.IR spectra of different complexes are given below.
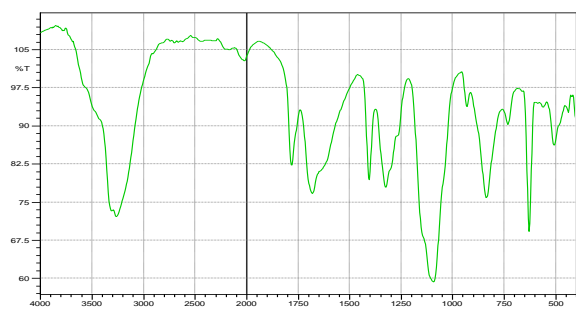

Fig:3. I.R. Spectra of Oxalatopent ammine Cobalt (III) perchlorate complex

The FT-IR Spectrum (Fig.3) of the complex displays bands at 3255 cm^{-1} that are indicative of the co-ordinate water. The strong bands at 1609 and 1500cm^{-1}, may be due to c=0 stretching band. The complex also exhibit bands at 1400, 1250, 1140, 800cm^{-1}

3.3 Kinetic study

The Kinetics of the oxidative degradation of Oxalatopentammine Cobalt (III) perchlorate complex by colloidal MnO$_2$ in acid medium was studied by varying concentration of the complex from 2.8 x10^{-4}- 4.8 x10^{-3}mol dm^{-3} ,colloidal MnO$_2$ from 1.6x10^{-5}-2.6x10^{-5} moldm^{-3}and HClO$_4$ concentration from 1.0x10^{-4}-1.0x10^{-3} moldm^{-3} .

3.3.1. Rate dependence on colloidal MnO$_2$

The order with respect to colloidal MnO$_2$ was determined by finding K$_{obs}$ at different initial concentrations of MnO$_2$ (1.6x10^{-5}-2.6x10^{-5} moldm^{-3}) with other parameters remaining fixed [HClO$_4$] = 1.0 x 10^{-4} mol dm^{-3} [complex] =2.8x 10^{-4} mol dm^{-3}. It has been found that the values of rate constants remained constant for all concentrations of colloidal MnO$_2$ (table-1). The constant values of rate constants indicate that the rate is independent on concentration of colloidal MnO$_2$. According to the basic tenets of chemical kinetics the pseudo-first order rate constants should be independent of the initial concentration of MnO$_2$. So the reaction is pseudo 1st order with respect to colloidal MnO$_2$.

3.3.2. Rate dependence on [HClO$_4$]

The order with respect to HClO$_4$was deduced from the values of k$_{obs}$ obtained at several [HClO4] (1.0 x10^{-4} to 1.0 x 10^{-3} mol dm^{-3}) with fixed [Coll.MnO2] (=1.6 x 10^{-5} mol dm^{-3}) and [complex] (=2.8x 10^{-4} mol dm^{-3}). The values of rate constant increased with increase in [HClO$_4$] indicates that the reaction is acid catalyzed. A plot of logk versus log [HClO$_4$] is linear with slope 0.5742 which confirmed that the reaction is less than first order with respect to [HClO$_4$] (fig.-4).

Table -1:- Effect of varing the [Colloidal MnO$_2$], [complex] and [HClO$_4$] on the pseudo-first order rate constants for the oxidative degradation of

Oxalatopentammine Cobalt (III) perchlorate by colloidal MnO$_2$.

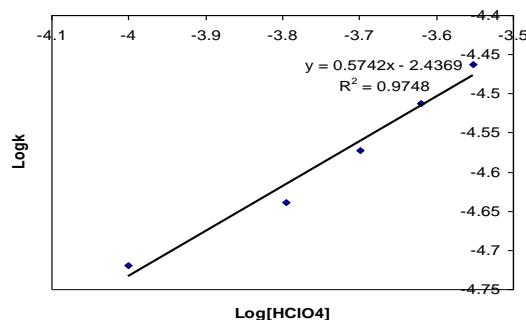| 10^5[MnO$_2$]moldm^{-3}	10^4 [complex] mol dm^{-3}	10^4[HClO$_4$]mol dm^{-3}	10^5 k$_{abs}$ sec^{-1}
1.6	2.8	1	1.91
1.8			1.91
2.0			1.91
2.2			1.91
2.4			1.91
2.6`			1.91
1.6	2.8	1	1.91
	3.2		2.30
	3.6		2.68
	4.0		3.07
	4.4		3.45
1.6	2.8	1.0	1.91
		1.6	2.3
		2.0	2.68
		2.4	3.07
		2.8	3.45

Fig.4. Log-log plot of concentration of Perchloric acid with rate constant

3.3.3. Rate dependence on [complex]

The order with respect to complex was deduced from the values of k$_{obs}$ obtained at several [complex] (2.8 x10^{-3} to 4.8 x 10^{-3} mol dm^{-3}) with fixed [Coll.MnO2] (=2.8 x 10^{-5} mol dm^{-3}) and [HClO$_4$] (=1.0x10^{-4} mol dm^{-3}). The values of rate constant increased with increase in [complex]. A plot of logk versus log [complex] is linear with slope 1.30741 which confirmed that the reaction is first order with respect to complex (fig.-5).
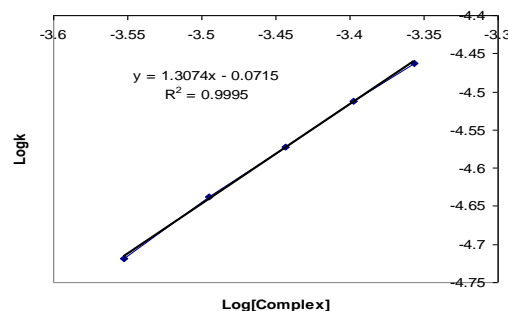

Fig.5. Log-log plot of concentration of Oxalatopent ammine Cobalt (III) perchlorate with rate constant

IV. CONCLUSION

The colloidal MnO_2 first prepared by Perez- Benito et al. can be used for the Oxidative Degradation of Oxalatopent ammine Cobalt (III) perchlorate Complex in acid medium. This oxidation process is a acid catalyzed reaction and obeys 1st order kinetics with respect to the complex and colloidal MnO_2.

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