Kinetics of the Oxidation of Mercaptosuccinic Acid by Methylene Blue Catalysed by Copper in Presence of Ru(III) in Acidic Medium

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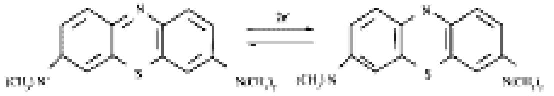
Abstract:** Kinetics of the oxidation of mercaptosuccinic acid by methylene blue ,the environmental factor considerably affect the reactivity by transition metal likeCu(II)in presence of Ru(III). Kinetic feature are very much different in presence of Cu(II) alone and Cu(II),Ru(III) simultaneously).In presence of Cu(II) alone the order follows first order kinetics with respect to methylene blue but on adding Ru(III) along with Cu(II), the order in MB changes to ½ under aerobic condition.We measure sample runs in aerobic and anaerobic condition.Dissolve oxygen in reaction mixture influence the order of reaction.The order is unity in TMA and in MB is fractional. The rate almost constant on increasing $[H^+]$ .The rate show positive effect of [Cu(II)], at higher [Cu(II)]rate changes from half to one and dependency unity to half .The slightly increases on increasing [Ru(III)]and show fractional dependency.The increase in dielectric constant rate increases, the variation in ionic strength with KCl,NaCl,$KNO_3K_2SO_4$,rate decreases but withNaCl,$KNO_3$and K_2SO_4 show transition from first order to zero order. The stoichiometry is found to be 2:1 between TMA and MB.The addition addition of oxidised product and leuco base slightly increases the rate .The activation parameter evaluated on increasing temperature ,rate decreases but at higher temperature the rate constant slightly increases,this shows anti-Arrhenius behaviour of the reaction.

***Keywords** -Mercaptosuccinic acid, methylene blue, anti-Arrhenius behaviour, anaerobic condition*

INTRODUCTION

Investigation of the chemistry of model systems at a molecular level is an important first step towards understanding the chemistry of the active site of enzymes [1]. Gas phase experiments are well established means for the investigation of both the intrinsic reactivity of organo-metallic system and role of electronic structure [2].The tendency of transition metal thiolates specifically those of Zinc, to form oligo-metric and polymeric species is well established [3-5] .Copper is an essential trace element which form an integral compound of many enzyme [6] while trace amounts of copper are needed to sustain life. Excess copper is extremely toxic .Although various aspects of copper transport and metabolic activity have been investigated in the past [7-11], very little is known about the specifics of intracellular copper transport [12]. Copper (I)-thiolate clusters are of significant interest because of their biological relevance to the cysteine rich copper (I).Proteins such as metallothioneins [13] copper regulatory proteins [14,15] and phytochelatins [16].The biological significance of sulphur compound especially thiols [17] has prompted the studies on metal catalysed electron transfer reactions involving sulphydryl substrates.The participation of metal ions in regulation of mitochondria electron transfer reactions is the basic component of cellular energy transduction and ATP synthesis.The supra molecular interaction of organic dyes with biological molecule has been increasingly used as study models of some biophysical processes and in understanding the functions of biological macromolecules [18].This is studies methylene blue (MB) which is a phenazine dye has been used as a oxidant. This chromato-phoric oxidant has been largely employed as an electron receptor in biochemical studies for the oxidation of flavin bound enzymes [19] and in understanding DNA cleavage [20]. The oxidation of some sulphur analogues substrate has been investigated in this laboratory [21-26]



Methylene blue has been used as a probing agent to investigate the depolymerisation of biopolymers by ultra-violet radiation [27], initiates photooxidation of number of substrate like L-methionine etc [28].A glimpse at these details indicates that chemistry of methylene blue is extremely significant in view of its multifacet reactivity and thus it has been used as principle reactant in our investigation.

MATERIALS AND METHODS

The solution of mercaptosuccinic acid (TMA,M/s Evans chemetics,Inc-USA and methylene blue (MB,M/s Merck Ltd, Germany) by exact weighed amount of the compound dissolve in acetone (Merck,GR) and doubly distilled water respectively. The solution was kept in the dark. All other reagents were either E.Merck GR or BDH AnalaR grade sample .The corresponding disulphide of TMA was prepared by oxidising it with hydrogen peroxide and extracting the product with ether. Dihydromethylene blue (leuco dye) was prepared using Sn-HCl couple .The progress of the reaction were followed spectrophotometrically using ATI-UNICAM UV2-100 spectrophotometer at 660 nm.The oxidant follows the Beer"s law in this concentration range currently employed. Anaerobic atmosphere was made by using nitrogen atmosphere.

RESULT AND DISCUSSION

The order of reaction in the methylene blue was determined by Oswald"s isolation method .A Series of runs were made at fixed concentration of MB (ca. $2.0x10^{-5}$M).and different TMA concentration, keeping all other kinetic parameter constant .The runs were made in aqueous- acetone medium (34%v/v) and in presence of hydrochloric acid (ca.$2.0x10^{-2}$M).(The variation between all the rate constant in each run resulted in C.Vs that was <5%). A rate constant consolidated in table -I at different TMA concentration

TMAx10^3M	$k_{1/2}$x10^6mol$^{1/2}$l$^{-1/2}$s^{-1}
0.6	1.69
0.8	2.30
1.0	2.60
1.5	3.51
2.0	4.85
2.5	6.27
3.0	8.55

Table I: [MB]=$2.0x10^{-5}$M;[HCl]=$2.0x10^{-2}$M;[$CuSO_4$]=$2.0x10^{-5}$M;[Ru(III)]=$2.0x10^{-6}$;[KCl]=0.1 M;Acetone=34%v/v;I=0.12M;Temp=35^0C

The half order rate constants obtain at different [TMA] with respect to methylene blue .A plot of log[TMA] against log k1/2 gives a straight line with a slope 1.03 .Number of runs were made at different [MB] keeping all other parameter constant. A plot of between log[MB] and log k1/2 gives a straight line with a slope of 0.33 which indicates that the concentration order in MB is almost equal to the time order.

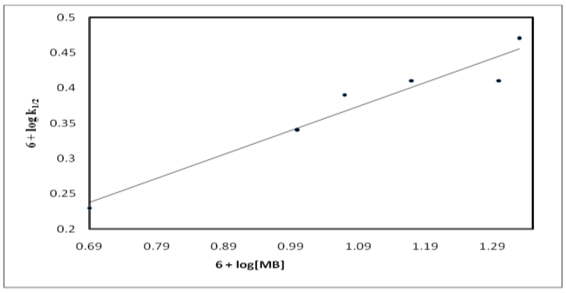


Figure-I: [TMA]=$1.0x10^{-3}$M;[HCl]=$2.0x10^{-2}$M;[$CuSO_4$]=$2.0x10^{-5}$ M;[Ru(III)]=$2.0x10^{-6}$M;[KCl]=0.1 M;Acetone=34%v/v;I=0.12M;Temp=35^0C

On increasing hydrogen ion concentration initially rate decreases then slightly increases

[HCl]x10^2M	$k_{1/2}$x10^6mol$^{1/2}$l$^{-1/2}$s^{-1}
0.5	2.89
1.0	1.98
1.5	1.86
2.0	2.16
2.5	2.10
3.0	2.05

Table-II:[TMA]=$1.0x10^{-3}$M;[MB]=$2.0x10^{-5}$M;[$CuSO_4$]=$2.0x10^{-5}$M;[Ru(III)]=$2.0x10^{-6}$M;Acetone=34%v/v;I=0.20M;Temp=35^0C

The concentration of Cu(II) ion act as a catalyst was varies by adding different volumes of the solution of copper sulphate their is change in order from half to one.A plot of log k_1 against Cu(II) gives a straight line with a slope equal to 0.83,similarly a plot of log $k_{1/2}$ vs Cu(II)gives a straight line with a slope of 0.39 which shows that the dependence of rate on Cu(II) changes on varying the concentration of the catalyst.The other catalyst Ru(III) concentration also show positive effect on the rate of reaction a double log plot between $k_{1/2}$ and Ru(III) gives a straight line with a slope equal to 0.35 which suggest that Ru(III) exert a synergetic effect on Cu(II).

The ion strength of system was not maintain constant because by adding of $CuSO_4$ produces an insignificant change in the ionic strength of system

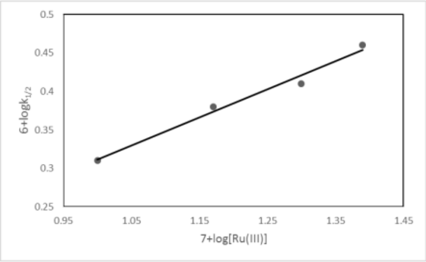


Fig-II:[TMA]=1.0×10^{-3}M;[MB]=2.0×10^{-5}M;[Cu(II)]=2.0×10^{-5}M;[HCl]=2.0×10^{-2}M;[KCl]=0.1 M;Acetone=34%v/v;I=0.12M;Temp=35^0C

Variation in dielectric constant by altering the acetone content of reaction mixture .The rate of reaction increases on increasing the dielectric constant of the medium.However at lower percentage of acetone reaction obeys a first order kinetics in MB. The ionic strength of reaction system was varies by adding the electrolyte such as KCl,NaCl and KNO_3.

The addition of oxidation product (disulphide of TMA) and leuco base negligible effect on the rate .The activation parameter of the reaction determine by change in temperature, the rate constant decreases on increasing the temperature tends to attain a limiting value, but at higher temperature adverse effect show.A plot was drawn between log $k_{1/2}$ and 1/T which gives a straight line with a positive slope at lower temperature, while a straight line with a negative slope is obtained at higher temperature this confirms the anti- Arrhenius behaviour of the reaction.

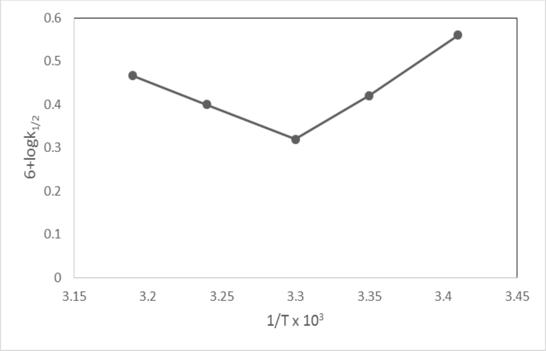


Fig-III:[TMA]=1.0×10^{-3}M;[MB]=2.0×10^{-5}M;Ru(III)]=2.0×10^{-6}M;[HCl]=2.0×10^{-2}M;[$CuSO_4$]=2.0×10^{-5} M;[KCl]=0.1 M;Acetone=34%v/v;I=0.12M;

The activation parameter was calculated by using the "Eyring equation" at higher temperature as well as lower temperature .At lower temperature reaction shows anti-Arrhenius behaviour whereas at higher temperature exhibit Arrhenius behaviour. For both segments of the reaction ,activation parameters were calculated in the usual manner.

Kinetic behaviour	ΔH* $kJmol^{-1}$	ΔS* J $deg^{-1}mol^{-1}$	ΔG* kJ mol^{-1}
Arrhenius	12.83	-313.79	109.5
Anti-Arrhenius	-15.50	-405.8	109.5

The reaction follows a half order kinetics in methylene blue under aerobic condition which changes to zero under anaerobic conditions.The rate in the substrate is one and the rate does not show any appreciable changes on varying hydrogen ion concentration .The addition of electrolytes also exhibits a diverse influence but considerably influence by medium.The half order rate constant shows a fractional dependence on the concentration of Cu(II) and Ru(III).These kinetic features suggest that the substrate mercaptosuccinic acid interacts with Cu(II) to form a labile coordination compound designated as C .This complex seems to coordinates with Ru(III) forming a mixed complex C'.This species C' may subsequently react with the protonated methylene blue is protonated in acidic medium [29-31] to form the reactive intermediate C*

$$\mathrm{RSH} + \mathrm{Cu^{II}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \quad \text{.......... (i)}$$

$$C + \mathrm{Ru^{III}} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} C' \quad \text{.......... (ii)}$$

$$\mathrm{MB} + \mathrm{H^+} \overset{K}{\rightleftharpoons} \mathrm{MBH^+} \quad \text{.............(iii)}$$

$$C' + \mathrm{MBH^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C^* + \mathrm{Cu^{II}} + \mathrm{Ru^{III}} + \mathrm{H^+} \quad \text{.. (iv)}$$

$$C^* \xrightarrow{k_3} H\dot{M} + R\dot{S} \quad \text{........(v)}$$

$$H\dot{M} + RSH \xrightarrow{\text{Fast}} R\dot{S} + H_2M \quad \text{... (vi)}$$

$$2RS^* \xrightarrow{\text{Fast}} RSSR \quad \text{.......... (vii)}$$

The formation of free radicals leading to deprotonation -

$$-\frac{d[\mathrm{MB}]}{dt} = \frac{k_1 k'_1 k_2 k_3 K [\mathrm{RSH}][\mathrm{Cu^{II}}][\mathrm{Ru^{III}}][\mathrm{MB}][\mathrm{H^+}]}{\left(k_{-2}[\mathrm{Cu^{II}}][\mathrm{Ru^{III}}][\mathrm{H^+}] + k_3\right)\left(k'_{-1}\left(k_1 + k'_1[\mathrm{Ru^{III}}]\right)\right) - k'_{-1}k'_1[\mathrm{Ru^{III}}]} \quad \text{........(viii)}$$

The rate expression(vii) explain first order kinetics in substrate and the fractional dependence on the concentration of metal ions as well as on the concentration of hydrogen ion.It seems that at higher concentration of the catalysts,the magnitude of k_3 increases appreciably in the denominator of equation giving a first order kinetics in methylene blue under these condition.In fact the order in MB becomes one at higher concentration of the catalyst which is in agreement with the proposed reaction scheme .It has been emphatically mentioned in the experimental part that the rate of reaction decreases on increasing the temperature conforming to anti-Arrhenius behaviour.The usual Arrhenius behaviour has been observed when the reaction has been investigated in presence of metal pair ion Cu(II) and Ru(III). It would be pertinent to mention here that extensive studies concerning the effect of systems comprising salts of transition metals and Nand S containing inhibitor on the liquid phases oxidation of hydrocarbons [32,33].In this case ,at higher temperature the reaction exhibits Arrhenius behaviour but at lower temperature the system is found to show anti- Arrhenius behaviour.It seems that ligation is appreciably influence by temperature,it is also reported in literature that Ru(III) is optically activated[34] and it seems that at higher temperature this activated metal ion acts as a catalyst.This may over power the retarding influence of temperature and lead Arrhenius behaviour for the reaction.Admittedly ,however this explanation is largely qualitative in nature.

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