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INFLUENCE OF NANOPARTICLES ON METAL ION CATALYZED OXIDATION OF MODEL SUBSTRATES BY METHYLENE BLUE IN ACIDIC MEDIUM

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Abstract: - The catalytic activity of metal ions is attributed to the formation and participation of metal nanoparticles in homogeneous – heterogeneous domain. Studies indicates a change in morphology of metal ion-substrate nanoparticles from nanorods to nanogranules on adding another metal ion to the reaction system. Metal ions have unique properties including redox/electron transfer and diverse oxidation states and coordination number due to which metal and metal compounds have tremendous potential and wide applications in various fields. The present paper highlights the interaction of bioactive sulfhydryl substrates, glutathione, cysteine hydrochloride and 2- mercaptoethylamine hydrochloride with methylene blue in acidic medium in a mole ratio of 2:1 forming the corresponding disulfide and dihydromethylene blue (leucobase) in acidic medium. In the present system the catalytic property of metal ions is due to the formation of nanpoparticles & their multifacet involvement in metabolic pathways have attracted considerable attention. Thus, these studies, on metal nanoparticle , catalysed oxidation of model substrates paves the way to understand the complex chemistry of such systems.

Keywords: metal ion catalysis, nanoparticles, model substrates.

INTRODUCTION

The concept of metal ion catalysis is not new but its immense application in various fields especially in metal-thiolate ligation has attracted a considerable attention mainly due to the multifacet involvement of these systems in metabolic pathways [1-7]. It has been realized that certain enzymes contain thiolate bridged assemblies of the general formula Fe_4S_4-(X) M in which Fe_4S_4 cubane is covalently linked to another metal ion by thiolate(s) or sulphides [8]. Recently, the use of nitrosyl radicals alone or in combination with transition metals as catalysts in oxidation processes has been exploited for synthetic as well as mechanistic view point [9]. It is also realized that the catalytic activity of metal ions in some cases is attributed to the formation and participation of metal nanoparticles in homogeneous – heterogeneous domain [10, 11]. It has been reported that addition of cesium (I) and rhenium (VII) ions remarkably increase the catalytic activity of homogeneous poly (acrylic acid)-stabilized silver (PAA-Ag) nanoclusters. Heterogeneous palladium nanoclusters, acting as a catalyst, were immobilized on chelate resin-metal ion complexes, and were prepared by reduction of palladium (II) ions supported on resin complexes [12]. The catalytic activity of nanoparticles is attributed to the existence of enormous number of active sites available to the reactants and the efficiency of nanoparticle catalyst is known to depend on various factors such as porosity, morphology , size ,phase composition,solvent etc.[13]. Metal ion catalysis involving participation of nanoparticles and sulfur chemistry have attracted considerable attention mainly due to the multifacet involvement of these systems in metabolic pathways. In the light of this, comparative metal ion catalyzed oxidation of bioactive sulfhydryl substrates by a model electron receptor methylene blue (MB) have been studied in acidic medium.

EXPERIMENTAL AND RESULTS

The solutions of the substrates ,oxidant - methylene blue (MB) and metal ions were prepared by dissolving an exactly weighed

quantity in double distilled water as already reported in earlier communications [14-15].The reaction mixture except methylene blue was thermostatted for half an hour and the solution of MB was subsequently added to the reaction system. Reaction vessels (Pyrex, England) coated black from outside with Black Japan were used. These were thermostatted (Julabo, Germany, variation ± 0.02°C) at the desired temperature for a sufficient length of time and the aliquots were analyzed at different time intervals at 664 nm on an ATI-UNICAM UV 2-100 spectrophotometer with the help of Beer- Lambert law plots for MB. The interferences due to leuco base and the disulfide are ruled out because these species absorb strongly in the uv region of the spectrum. The oxidation product i.e. the corresponding disulfide was prepared by oxidizing the respective thiols with hydrogen peroxide [16] and recrystallizing it in water-methanol mixture. Dihydromethylene blue was prepared by reducing methylene blue with Sn-HCl couple as described earlier [17].

In all the cases the stoichiometry of the reactions was determined analytically as well as spectrophotometrically. The UV-visible and IR spectra of the substrates, the known samples of the reaction products viz. the disulfide and the leuco base and those recorded for reaction systems after completion of the reaction were compared. This indicates that two moles of the substrates interact with one mole of methylene blue forming the corresponding disulfide and the leuco base (H_2M) :

$$2RSH+MB \longrightarrow RSSR+ H_2M$$

Different metal ions show different behavior in the presence of dissolved oxygen for example in oxidation of both the substrates cysteine , 2-ME by MB, the kinetics of Cu(II)-catalyzed reaction were found to be very much influenced by dissolved oxygen[14,15,18]. Similarly in case of ruthenium catalysed oxidation of glutathione the rate is very much influenced by the dissolved oxygen[14]. However, on adding Zn(II) to the reaction system, an identical behavior was noticed under aerobic and anaerobic conditions that indicates the kinetic significance of Zn(II) in these reaction systems.

In the experimental section kinetic studies were carried out for different substrates using different metal ions and the results and role of nanoparticles were compared. in all the cases the order in the oxidant was determined by Ostwald's isolation method for which a series of runs were made with different concentrations of the substrate and fixed concentration of oxidant. This was again confirmed by the graphical method and by the van't Hoff differential method. The order of the reaction varies from zero to two in different substrates .The order in the substrate was measured by the initial rate measurement method and confirmed by graphical method . in the similar manner the variation in the concentration of H^+ ions , metal ions has been studied for all these redox systems . These reactions show an incoherent behaviour on varying the ionic strength which may be attributed to an environmental effect. The rate increases on increasing the dielectric constant of the medium. In the oxidation of cysteine, the rate increases on increasing the concentration of Cu(II) and the plot of log $k_{1/2}$ against log [Cu(II)] gives a straight line with a slope of 0.6. This is in contrast with the observations made for Cu(II)- catalyzed oxidation of this substrate[18] where the rate slightly increases on increasing [Cu(II)] and subsequently attains a limiting value at higher concentrations of Cu(II). This again highlights the specific mode of participation of metal ions acting as catalysts in these systems. In case of glutathione the rate constant increases linearly on increasing the concentration of Ru(III).The double log plot between k_0 and Ru(III) gives a straight line with

a slope of 0.96 . The rate of reaction is not influenced by the time of equilibration of the catalyst with other ingredients of the reaction system excluding MB which is in contrast with the observations made for Ru(III) catalyzed oxidation of cysteine with this oxidant [15].The addition of the corresponding disulfides did not produce a change in the rate. The rate of reaction again remains unaffected on adding dihydromethylene blue to the system in the oxidation of cysteine whereas in the oxidation of 2-ME, the rate of reaction slightly decreases with increasing the concentration of leuco base. The time of equilibration of the metal ion with other ingredients of the reaction system did not affect the rate in 2-ME.

The activation parameters of the reactions were evaluated by making the runs at different temperatures ranging between 25 and 45°C. ΔH*, ΔS*and ΔG* for the oxidation of cysteine ,2-ME and glutathione were calculated by the use of Eyring equation, van't Hoff isochore equation and by using Arrhenius plots. These were compared and it was found that all these oxidation reactions are accompanied by the negative entropy of activation.

DISCUSSION

Rate equation has been formulated for all these systems by considering the protonation of MB to MBH^+ and the coordination of substrate with a metal ion to form an unstable complex formed in situ. It seems that this complex C_1 perhaps facilitates an intramolecular rearrangement in the substrate molecules as a consequence of the participation of nanoparticles. Complex C_1 may interact with protonated methylene blue molecule (MBH^+) to produce a transient species C* while Cu(II) , hydrogen ion and (Zn (II) are liberated. The transient species C* may subsequently dissociate to give radicals $RS^{\cdot}$ and $HM^{\cdot}$ (half reduced methylene blue radical) which in turn, may interact with the substrate molecule to give the end products. Incidentally, the participation of radicals such as $RS^{\cdot}$ and $HM^{\cdot}$ in these reaction systems has been frequently reported in the literature [19,20]. By considering the formation of C* as a rate determining step and applying the steady state treatment for the transient species the rate of reaction is given by [18]

$$-\frac{d[MB]}{dt} = k_1[RSH]\,[Cu(II)]\left\{\frac{k_{-1}\,[H^+]\,(k_3\,K\,[MB]\,[H^+] + k_{-2}) + k_2k_3\,K\,[Zn(II)]\,[MB]}{k_{-1}\,k_3\,K\,[MB]\,[H^+] + k_{-1}k_{-2}\,[H^+] + k_2k_3\,K\,[Zn(II)]\,[MB]}\right\} \qquad (14)$$

and for Ru(III) catalysed oxidation of glutathione ,the rate is given by [14]

$$-\frac{d\,[MB]}{dt} = \frac{3k_1\,K_1^{2/3}K_2\,[RuIII\,]\,[RSH]}{[H^+]} \qquad (21)$$

These rate equations explain almost all the characteristic feature of the reaction system. Formation of nanoparticles within the reaction system plays a very important role in metal ion catalysed redox systems. Among various metal particles copper nanoparticles are attracting a greater attention because of their optical , catalytic and electrical conducting properties at a significantly lower cost than gold and silver. Copper nanoparticles being cheaper , require mild conditions for high yield of products in a short time as compared to a traditional catalyst and can be exploited in many industrially important reactions such as Biginelli reaction, in the reduction of aromatic nitro compounds to aromatic amino compounds in the presence of tetra hydro furanes THF/H2O and sodium borohydride in the synthesiss of 2-arylbenzoxazoles by the coupling of aromatic or heteroaromatic aldehydes with 2- aminophenol through the oxidative cyclization of the Schiff's base using Cu nanoparticles in the presence of

K_2CO_3 in methanol etc. so Cu will gain increasing importance as it is expected to be an essential component in the future nano devices due to its excellent conductivity as well as good biocompatibility and its surface enhanced Raman scattering activity [21]. In the present case, the catalytic activity of Cu(II) is due to the formation of Cu-cysteine nanorods as revealed by transmission electron microscopy. Zn-cysteine interaction also gives indications of the formation of nanoparticles but they are low-melting and thus, could not be characterized. It has already been recorded that the morphology of the nanoparticles changes in presence of Zn (II) and nanogranules are obtained. Glutathione (γ-glutamylcysteinylglycine) which is an important bioactive sulphydryl compound protects the –SH group of different proteins and enzymes from oxidation, deactivation and radiation injury besides being a model system for the binding of metal ions especially those involved in the toxicology. Recently glutathione (GSH) - decorated magnetic nanoparticles for binding glutathione-s-transferase (GST) fusion protein and manipulating live cells have been prepared [22] . Studies on cosensitization properties of GSH- protected Au_{25} clusteron ruthenium dye –sensitized TiO_2 photoelectrode suggests that GSH- protected Au_{25} clusters should behave as both a coadsorbent to increase active sensitizer, which opens new methodologies for the design of coadsorbents with sensitization properties [23]. In addition to this nanoparticle based delivery and release system using GSH as the releasing agent can be further utilized to realize delivery of proteins and enhance transfection of genetic materials [24].These studies with different view point clearly highlights the importance of metal ion catalysed oxidation of model substrates which is basically due to the formation and participation of nanoparticles & this paves way for further studies in the future.

CONCLUSIONS:

The reaction between substrates cysteine hydrochloride , 2- mercaptoethylamine hydrochloride and glutathione by methylene blue catalyzed by metal ions in acidic medium shows the formation and participation of nanoparticles. Studies indicates a change in morphology of metal ion-substrate nanoparticles from nanorods to nanogranules on adding another metal ion to the reaction system. It has already been mentioned by Komalam and coworkers that these metal nanoparticles helps the electron relay from the donor to the acceptor. The particles possess large surface area which acts as the substrate for the electron transfer reaction. Just before the electron transfer reaction both of the reactants are adsorbed on the metal particle . Subsequently the reactant gains an electron and is reduceed . Thus, the metal particles act as an efficient catalyst in the electron transfer process. Such studies on metal nanoparticle catalysed oxidation of model substrates paves the way to understand the complex chemistry of such systems.

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