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# Kinetics of Oxidation of L-Cysteine by Transition Metal Complexes

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Kinetics of the oxidation of L-cysteine by chromium(III), manganese(III), iron(III), and cobalt(III) complexes of amine, 2,2′-bipyridine, ethylenediamine, acetylacetonate, N,N′-bis(salicylidine)-1,2-ethylenediamine and (1R, 2R)-(-)-N,N′-bis(3,5-di-*t*-butyl-salicylidene)-1,2-cyclohexyldiamine have been studied spectrophotometrically. Kinetics measurements were run under pseudo-first order conditions in which the concentration of cysteine is between one and two orders of magnitude greater than that of the transition metal complex. Measurements were done in aqueous and water ethanol solutions at 25°C, pH = 7 and an ionic strength of 0.20 M. The orders of the reaction with respect to both cysteine and the transition metal complex were determined. The observed rate constants and the overall rate constants were measured. It is found that the rate of oxidation depends on the metal centre and on the geometry of the complex. It also depends on the nature of the ligand, related to its degree of conjugation, number of coordination sites, size and strength in the spectrochemical series. The effect of the solvent and other variables on the rate of the reaction were studied and discussed.

**Key Words: Kinetics, Catalysis, Oxidation, L-Cysteine, Metal complexes.**

## INTRODUCTION

Oxidation of amino acid by a transition metal complex is of great importance structurally, catalytically and biologically. The oxidation reaction involves electron transfer reaction of the metal complex, which is an important process in coordination chemistry. The reaction has been studied by different methods, including: stopped-flow spectrophotometry, chemical analysis of products and the use of radioactive and stable isotope tracers. Discussion of these methods, along with much of the data produced and interpretation of the results according to different pathways in this field, is given elsewhere[1]. Several investigators reported studies on the oxidation process of several amino acids by various transition metal complexes[2–10]. Kinetics and mechanism of oxidation of L-methionine by 1,10-phenanthroline iron(III) complex in perchloric acid medium have been studied by Vani *et al.*[2] Sharma *et al.*[3] reported the reactivity of iron(V) and iron(VI) with

glycine and α-alanine using stopped-flow and pulse radiolysis techniques at pH 12.4 and 23–24°C. Laloo *et al.*[4] studied the kinetics of oxidation of three amino acids (lysine, arginine and histidine) by alkaline hexacyanoferrate(III) at constant ionic strength over the temperature range 318–338 K. Jameson *et al.*[5, 6] reported anaerobic oxidation of cysteine to cystine by iron(III) in acidic solution using stopped-flow high-speed spectrophotometric method. The oxidation of amino acids, in the presence of Os(VIII) as a catalyst, by alkaline hexacyanoferrate(III) to aldehydes has been reported by Mehrotra *et al.*[7] Of particular interest and relation to the present work, Abdel-Halim *et al.*[8–10] reported recently kinetics measurements of oxidation of L-cysteine and proline by some cobalt(III) and iron(III) based complexes containing various ligands such as CN, $NO_2$, acac, $NH_3$, urea, 1,2-diaminoethane and 1,10-phenanthroline. They investigated the effect of the nature of the ligand, in the transition metal complex, on the rate of oxidation of cysteine.

In the present work, complexes with Schiff base ligands containing N and O as donor atoms (known as salens) are employed in the kinetic studies. Such complexes have been used as catalysts for epoxidation, oxidation and polymerization of olefins and other organic substrates[11–13]. Chiral salen complexes were applied in asymmetric catalytic and electrochemical catalytic reactions. In asymmetric catalytic reactions, both the geometry and redox potential of the chiral salen metal complexes affect enantioselectivity[14]. The influence of the geometrical features and electronic properties in Schiff base metal complexes on the catalysis of oxidation of some organic compounds and in organic synthesis, stimulated us to study their behaviour in the oxidation process of amino acids.

As an augmentation to our previous studies on amino acids oxidation[8–10] and on our studies on the coordination chemistry of heteroatom-containing ligands[15, 16] and their catalytic applications[17, 18], we report on the kinetics of the oxidation of L-cysteine by chromium(III), manganese(III), iron(III) and cobalt(III) based complexes of various nitrogen and nitrogen-oxygen donor ligands. The observed rates and the rate constants of oxidation processes are given. Effect of various parameters on the oxidation rate is discussed.

## EXPERIMENTAL

L-cysteine (99%) was purchased from BDH and was used without further purification. The complexes $[Co(NH_3)_4CO_3]NO_3$ **(1)**[19], $[Co(NH_3)_5Cl]Cl_2$ **(2)**[20], *trans*-$[Co(en)_2Cl_2]Cl$ **(3)**[21] and *cis*-$[Co(en)_2Cl_2]Cl$ **(4)** (en: 1,2-diaminoethane), $[Co(bipy)_3]Cl_3$ **(5)**[22], and $[Fe(bipy)_3]Cl_3$ **(6)**[22] (bipy = 2,2′-bipyridine) were prepared following literature procedures. The iron(III)- and cobalt(III)-Schiff base complexes: [Fe(salen)Cl] **(7)**, [Mn(salen)Cl] **(8)**, [Fe(salen)(acac)] **(9)** (salen: N,N′-bis(salicylidine)-1,2-ethylenediamine) were prepared by the reaction of stoichiometric amounts of ligands with $MCl_3$ or $M(acac)_3$ (M = Fe or Mn) in alcohol and recrystallized using the appropriate solvents[23, 24]. [Mn(*ch*-salen)Cl] **(10)** (99.5%) and [Cr(*ch*-salen)Cl] **(11)** (99.5%) (*ch*-salen = (1R,2R)-(-)-N,N′-bis(3,5-di-*t*-butyl-salicylidine)-1,2-cyclohexyldiamine) were purchased from Strem Chemicals.

**Kinetic measurements:** Freshly prepared aqueous solutions of the desired concentrations of complexes and of cysteine were used for the kinetic measurements. The measurements were carried out using Cary 100 UV-Vis spectrophotometer from Varian Instruments. The reaction was monitored by following the change in absorbance of the transition metal complex with time at a predetermined wavelength; this wavelength was determined by recording the absorption spectral curves, for the complexes and for its mixture with cysteine (Cys) after the completion of the reaction. The reaction progress was monitored at the wavelength of maximum absorbance *difference* ($\lambda_{max}$) between the absorption of complexes and that of the mixture at the end of the reaction, and the reaction rate was measured at this wavelength. List of $\lambda_{max}$ for various complexes is shown in Table-1. All oxidation reactions were studied under pseudo-first order conditions. The concentrations of Cys used [$10^{-2}$–$10^{-1}$ mol $dm^{-3}$] were chosen to be 1–2 orders of magnitude larger than that of the complexes [$10^{-4}$–$10^{-2}$ mol $dm^{-3}$]. For salen complexes, due to their low solubility in water, the complex was dissolved in ethanol. The kinetic measurements were run in water-ethanol mixture. The ionic strength of the solutions was kept constant at 0.20 mol $dm^{-3}$ using $NaClO_4$. The temperature of the solution and its pH were both maintained at 25 ± 0.1°C and 7.0 ± 0.1, respectively.

TABLE-1
RATES OF OXIDATION OF CYSTEINE BY VARIOUS TRANSITION METAL COMPLEXES IN AQUEOUS MEDIUM AT 25°C, pH = 7.0 AND IONIC STRENGTH = 0.20 mol $dm^{-3}$

| No. | Complexes | $\lambda_{max}$ (nm) | k* ($dm^3$ $mol^{-1}$ $s^{-1}$) |
|---|---|---|---|
| 1 | $[Co(NH_3)_4CO_3]NO_3$ | 450 | $4.40 \times 10^{-5}$ |
| 2 | $[Co(NH_3)_5Cl]Cl_2$ | 440 | $1.27 \times 10^{-2}$ |
| 3 | *Trans*-$[Co(en)_2Cl_2]Cl$ | 400 | $1.72 \times 10^{-2}$ |
| 4 | *cis*-$[Co(en)_2Cl_2]Cl$ | 400 | $5.32 \times 10^{-5}$ |
| 5 | $[Co(bipy)_3]Cl_3$ | 400 | $9.04 \times 10^{-1}$ |
| 6a | $[Fe(bipy)_3]Cl_3$† | 520 | $1.64 \times 10^{-1}$ |
| 6 | $[Fe(bipy)_3]Cl_3$ | 520 | $7.35 \times 10^{-2}$ |
| 7a | [Fe(salen)Cl] † | 494 | $5.13 \times 10^{-2}$ |
| 7 | [Fe(salen)Cl] | 494 | $2.15 \times 10^{-2}$ |
| 8 | [Mn(salen)Cl]† | 387 | $4.04 \times 10^{-2}$ |
| 9 | [Fe(salen)(acac)]† | 400 | $4.24 \times 10^{-2}$ |
| 10 | [Mn(*ch*-salen)Cl] † | 415 | $1.27 \times 10^{-3}$ |
| 11 | [Cr(*ch*-salen)Cl]† | 415 | $8.69 \times 10^{-4}$ |

*Experimental errors are estimated to be 20%.
†Kinetic measurements were done in water-ethanol mixture.

## RESULTS AND DISCUSSION

Oxidation of cysteine (RSH) leads to formation of cystine (RSSR), as shown below[25]:

$$2RSH \rightarrow RSSR + 2H^+ + 2e^- \quad (1)$$

Estimation of residual oxidant suggested that 2 mol of cysteine consumed 2 mol of the complexes, $[M(III)\ L_n]^{m+}$, where M is the transition metal, such that

$$2[M(III)L_n]^{m+} + 2RSH \rightarrow 2[M(II)L_n]^{(m-1)+} + RSSR \quad (2)$$

where n is the number of ligands (L) around M(III) and m is the charge on the M(III)L complex.

The rate of the reaction is given by

$$\text{Rate} = k[Cys]^a[\text{complex}]^b \quad (3)$$

where k is the reaction rate constant and a and b are the orders of the reaction with respect to the concentration of Cys and complex, respectively. It was found that the rate is, in general, dependent on the first power of both the concentrations of substrate and oxidant, *i.e.*, $a \approx b \approx 1$, in agreement with previous studies[2, 4, 8-10] Since M(III) complexes are all one-electron oxidants, the oxidation of cysteine would give a radical intermediate, and the following mechanism is proposed:

$$RSH \Leftrightarrow RS^- + H^+$$

$$RS^- \rightarrow RS^\bullet + e^-$$

$$2RS^\bullet \rightarrow RSSR \quad (4)$$

with the second step is the rate-determining step.

At pseudo-first order conditions, in which [Cys] ≫ [complex], the concentration of the cysteine is essentially constant throughout the reaction. The reaction rate is then given by

$$\text{Rate} = -\frac{d[\text{complex}]}{dt} = k_{obs}[\text{complex}] \quad (5)$$

where $k_{obs}$ is the observed rate for the reaction, given by

$$k_{obs} = k[Cys] \quad (6)$$

where k is the second-order rate constant, in units of $dm^3\ mol^{-1}\ s^{-1}$.

For a first-order dependence of the reaction on [complex], the experimental absorbance-time data pairs were fit to the exponential function:

$$A_t = (A_0 - A_\infty)\exp(-k_{obs}t) + A_\infty \quad (7)$$

where $A_t$ is the absorbance of the TMC at time t through the reaction, $A_0$ is the initial absorbance of the complex (t = 0) and $A_\infty$ is the final absorbance of the reaction mixture at the end of the reaction ($t = \infty$).

The value of $k_{obs}$ (in $s^{-1}$) can be obtained from a plot of ln ($A_t$) *vs.* time. A plot of $k_{obs}$ *vs.* [Cys] gives the value of the second-order rate constant, k. Kinetics results for the oxidation of cysteine by various transition metal complexes are shown in Table-1.

Table-1 shows a wide variation in the oxidation rate of cysteine by the various complexes. Variations are attributed to several factors related to the structure of the complexes (Figs. 1 and 2). Among them: (a) the metal centre, (b) the nature of the ligand (number of coordination sites, degree of conjugation, size and

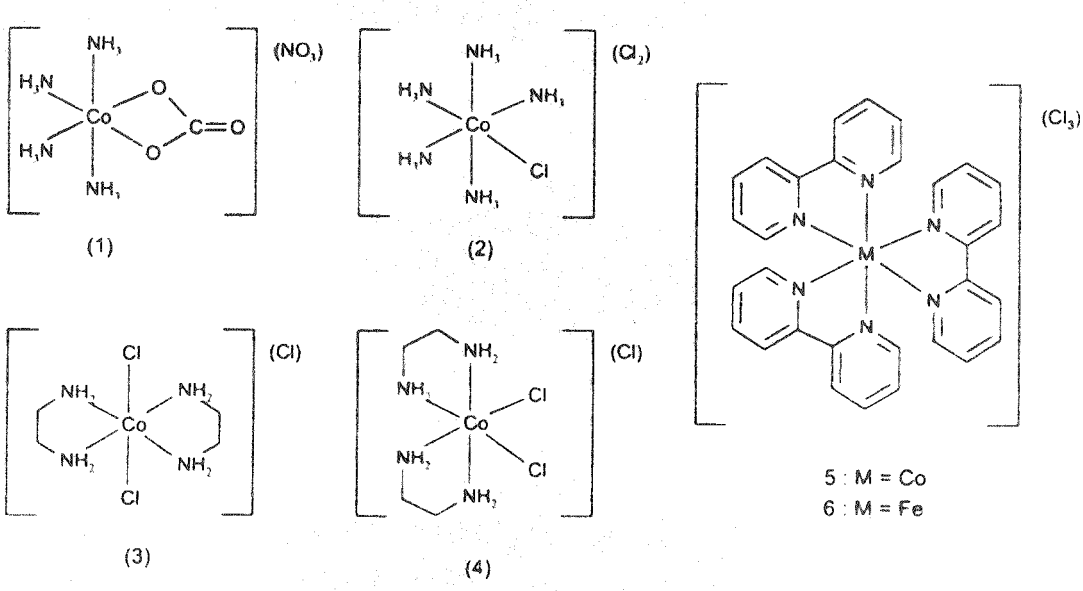


Fig. 1.

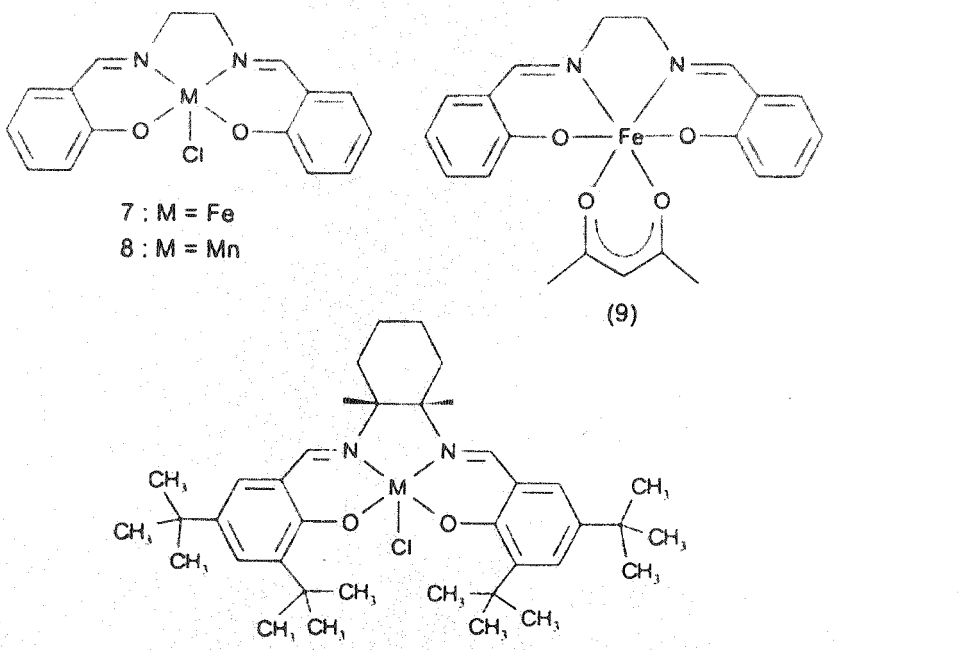


Fig. 2.

strength in the spectrochemical series), and (c) the geometry around the metal ion (*cis* or *trans*).

Deciding which mechanism the oxidation process of cysteine by a transition metal complex will proceed may be difficult. If a ligand in the complex has extra lone pair(s) with which to form "links" to cysteine and if the geometry around metal centre have enough space for cysteine to bound to this ligand, then the reaction is more likely to proceed *via* inner-sphere mechanism. In this case, a substitution reaction that leaves cysteine and the metal complexes linked by the bridging ligand, and the actual transfer of the electron is frequently accompanied by transfer of the ligand followed by separation of the products. However, when the ligands in the metal complexes have *no extra* lone pairs with which to form bonds to cysteine, or when there is a "closed" or crowded geometry around the metal centre, then the ligands are tightly held and there is no change in the coordination sphere on the reaction; the reaction proceeds by outer-sphere electron transfer[26]. By considering the nature of ligands and structures of metal complexes studied in the present work (Figs. 1 and 2) suggests that reactions are *most* likely to proceed *via* outer-sphere mechanism for metal complexes (**1–6** and **9–11**). Complexes **1–6** and **9** have *closed* octahedral geometries that do not permit linking between cysteine and metal complex. We also believe that the crowded square-pyramidal geometry around metal in complexes **10** and **11**, with four *t*-butyl groups, prevents inner-sphere pathway for the oxidation process.

Complexes **7** and **8** with square-pyramidal geometries, having vacancies for inner-sphere approach. However, it is unlikely for Cys, an electron-rich donor, to form a bridging bond to chloride, another donor. Also, according to Meyer and Taube[1], an inner-sphere redox reaction requires two metal centres, which is not present for the redox reaction of metal complexes **7** and **8** (and for the rest of the metal complexes). Therefore, we believe that *all* reactions studied in the present work proceed *via* outer-sphere mechanism.

For oxidation of cysteine by metal complexes in the present study, the primary change on electron transfer is a change in bond distance. A higher oxidation state on the metal leads to shorter σ bonds. The change in bond distance is larger when $e_g$ electrons are involved. Since the $e_g$ orbitals are anti-bonding, addition of electrons to these orbitals results in a less stable compound and longer bond distances [Co(III) complexes]. The combination of ligand-field energy change and stronger bonds to the ligands with stronger fields than water make the reaction easier. As a result, the rate of oxidation of Cys by metal complexes depends on the electrode potential for reduction of the M(III) complex.

Considering the nature of the ligand, Table-1 reveals that the rate constant for the oxidation of cysteine varies widely with the type of ligand in metal complexes. For outer-sphere reactions, the rate of electron transfer in a complex, $(ML_n)^{m+} + e^- \rightarrow (ML_n)^{(m-1)+}$, should depend on the nature of the ligand in addition to many other factors (*e.g.*, the match of energy levels of the two reactants and the solvation of the two reactants); different ligands cause different polarizabilities to the metal ion. Thus, the nature of the ligand determines the ability of the electron(s) to tunnel through the complex to reduce the metal ion, *i.e.*, the electrode potential of the complex. The presence of different ligands in

the complex causes different electrode potentials for $M^{3+}$ reduction. There are two reasons that affect the reduction potential of the $M^{3+}$ complex ion. *First*: ligands with $\pi$ electrons ($\pi$-donors or $\pi$-acceptors) provide better pathways for tunneling, and hence facilitate the reduction process. Therefore, it is expected that redox reaction rate should be faster with $\pi$-electrons ligands than with $\sigma$-donor ligands, or ligands with no extra lone pairs and no low-lying antibonding orbitals. However, the rate of electron transfer through ligands with strong $\pi$-acceptor effect is expected to be slower than the transfer rate through weaker $\pi$-acceptor ligands or $\pi$-donor ligands. The presence of vacant $\pi^*$ in strong $\pi$-acceptor ligands makes electron transfer harder. This is due to the possibility of the electron getting "trapped" or "captured", momentarily, in the vacant $\pi^*$ of the ligand. This is unlikely to occur in electrons "rich" $\pi$ or $\sigma$-donor ligands. Due to the possibility of back bonding, strong $\pi$-acceptors are also strong ligands. For an octahedral symmetry the splitting, $\Delta_0$, in the *d*-orbitals depends on the ligand strength. For a strong ligand with high $\Delta_0$, the donated electron, from cysteine, goes to the higher energy $e_g$ orbitals [Co(III) complexes]. This should be more difficult and less probable to occur than donation to the lower energy $t_{2g}$ orbitals for weak ligand. Therefore, one can conclude that the electrode potential of the metal ion becomes less positive, hence the redox rate should decrease as the ligand strength in the spectrochemical series increases.

The *second* factor that affects the reduction potential of $M^{3+}$, and hence the rate of the redox reaction, is the size of the ligand. As mentioned above, the rate of reduction of the metal ion in the complex depends on the ability of the electron to tunnel through the ligand. The probability of an electron to tunnel through the ligands is a quantum mechanical property, which can be calculated from time-dependent perturbation theory. Using Gamow equation, Abdel-Halim[27] derived a formula, which correlates the size of the ligand (x) to the transition probability. The probability of transfer for an electron leaking through a potential energy barrier across the ligand around the central metal ion is given by

$$\kappa = \exp\{-(8\pi d/3h)[2m(U - W)]^{1/2}\} \tag{8}$$

where $\kappa$ is known as the transmission coefficient, U is the height of the potential barrier, W is the kinetic energy of the electron, m is the electron mass and d is the width of the barrier at the height of penetration. As an approximation, one may consider U to represent the potential of an electron moving in the coulomb field of two ions. Therefore, U is given by the Coulomb equation

$$U = \frac{q_1 q_2}{Dd} - \frac{eq_1}{Dx} - \frac{eq_2}{D(d - x)} \tag{9}$$

where $q_1$ and $q_2$ are the charges of each of the ions [M(III) complex and cysteine, respectively], D is the dielectric constant of the solvent and (x) is the distance the electron has to travel from the electron donor (cysteine) to the centre of the electron acceptor [M(III)]. This distance depends on the size of the ligand around the central metal ion. The net charge on cysteine, $q_2$, is zero. Therefore, equation (9) reduces to the simple form

$$U = -\frac{eq_1}{Dx} \tag{10}$$

Equations (8) and (10) show that, for all other factors being the same, as size of the ligand in the complex increases, transmission coefficient and hence the rate constant should decrease.

Looking at the metal complexes studied (Table-1 and Figs. 1 and 2), one may classify them into three categories: (a) simple monodendate ligands (**1** and **2**), (b) bidendate ligands (**3, 4, 5** and **6**) and (c) bulky tetratendate ligands (**7, 8, 9, 10** and **11**). Comparing rates of oxidation of cysteine by complexes **1** and **2**, Table-1 shows the rate constant of oxidation of cysteine by **2** is more than two orders of magnitude larger than that by **1**. This can be attributed to the differences of the ligands Cl and $CO_3$. In agreement with eqn. (8) above, the relatively bulky size of $CO_3$, bounded to Co(III) in two positions, makes it harder for electron transfer to occur. Another reason that may contribute to difference in oxidation rates between **1** and **2** is the presence of ligands with different strength in the spectrochemical series, $CO_3$ and Cl, respectively. Even though complexes **1** and **2** have ligands with different coordination sites around Co(III), but one may compare rates in relation to ligand strength. Complex **2** having Cl is weaker than $CO_3$ in **1**, having faster oxidation rate with cysteine. This is in agreement with our previous findings[8, 9, 27]; the rate of oxidation increases as the ligand strength in the spectrochemical series decreases.

The effect of the size of the ligand can also be applied to explain the difference in rates of oxidation of Cys by *cis*- and *trans*-ethylenediamine complexes of Co(III) (**3** and **4**). The crowded *cis* isomer hinders a close approach of Cys making electron transfer harder, resulting in a rate of oxidation more than two orders of magnitude smaller than that for the *trans* isomer.

Complexes **5** and **6** have identical structures but differ in metal ion centre. The electrode reduction potentials ($E^\circ$) for Co(III) and Fe(III) explain the rate difference. The values of $E^\circ$ for Co(III) and Fe(III) are +1.81 V and +0.77 V, respectively. Thus, the rate constant of oxidation of Cys by Co(III) complex is more than ten times faster than that by Fe(III) complex.

To understand variations of rates for the rest of metal complexes, one needs to consider the effect of the solvent on reaction rate. Kinetics of oxidation by metal complexes **6a**, **7a** and **8–11** with Cys were studied in water-ethanol mixture. To study the effect of solvent on oxidation rate, kinetic measurements were done for two iron(III) complexes in water and in ethanol (**6a** and **6** and **7a** and **7**). In both cases, rates are higher in ethanol. Water, being highly polar, enclaves the metal complexes and thus hinders electron transfer from cysteine making the oxidation process slower.

Comparing the oxidation rates of *salen* complexes of Fe(III) and Mn(III), Table-1 shows that k for complexes **7a** and **8** is *almost* the same within our experimental errors. The presence of ethanol, which facilitates the redox reaction, minimizes the effect of the metal centre on the reaction rate.

As mentioned earlier, complexes **9, 10** and **11** have special catalytical and industrial importance. Complexes **10** and **11** differ in the metal centre. Comparing their oxidation rates with cysteine shows that k is smaller for metal complexes **11**. Even though the presence of ethanol minimize the metal centre effect, the difference in reduction potentials of Cr(III) and Mn(III) should affect rates. The

negative electrode potential for Cr(III) [E° for Cr(III) = –0.41 V] compared to the positive electrode potential for Mn(III) [E° for Mn(III) = +1.49 V] explains the higher rate for **10.**

To investigate the effect of the nature of the ligand, one may compare the oxidation rates of cysteine by metal complexes **6a** with **9**. Both have the same geometry, $O_h$, and the same metal center [Fe(III)]. The highly conjugated system of complex **6a** enhances electron transfer to cysteine from all orientations. This explains why the oxidation rate is the highest with complex **6a.**

The effect of the degree of conjugation in the ligand can also be observed by comparing rates with metal complexes **8** and **10.** Complex **10** has four non-conjugated and bulky *t*-butyl groups. This hinders electron transfer and slows oxidation rate.

Another comparison one can make is to compare rates of cysteine oxidation by Co(III) complexes **(1–5).** Even though the comparison here is difficult, due to presence of ligands with different coordination sites around Co(III), however, effect of conjugation is clearly observed. Complex **5** has the highest observed rate due to the presence of the conjugated bipyridyl group.

In summary, one may conclude that the rate of oxidation of cysteine by different transition metal complexes is found to depend directly on the electrode potential of the metal ion and the degree of conjugation of the ligand. The effect of degree of conjugation in the ligand is found to be predominant. The rate depends inversely on the size and the strength of the ligand. Also, the rate was found to depend on the geometry of ligands around the metal centre. Studying the effect of solvent indicates a drop in rates as the polarity of the solvent increases. In general, factors, which facilitate electron transfer, increase oxidation rate.

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