Indian Journal of Chemistry
Vol. 37A, May 1998, pp 413-417

Catalytic activity studies of some new transition metal complexes in the oxidation of ascorbic acid to dehydroascorbic acid

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Received 10 December 1997; revised 6 February 1998

Certain new Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde have been screened for their catalytic activity towards the oxidation of ascorbic acid. Results of the screening studies indicate that among the various metal complexes synthesised, only the Cu(II) complexes are highly efficient catalysts towards oxidation of ascorbic acid although a few other complexes also exhibit slight activity. The kinetics of oxidation of ascorbic acid in the presence of Cu(II) complex of the Schiff base quinoxaline-2-carboxalidene-2-aminophenol have been studied in detail in methanol water mixtures. These studies indicate that the reaction is first order in catalyst and zero order in ascorbic acid. Added ligand retards the reaction. A suitable mechanism has been proposed to explain these results.

Ascorbic acid, an important reducing agent in biochemical systems, is easily oxidized by many transition metal centres to dehydroascorbic acid[1-3]. A number of reports are available on the oxidation of ascorbic acid[4-11] catalysed by Cu(II) and Fe(III) ions and their complexes. We have synthesised and characterised certain new Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde[12]. All these complexes were screened for their catalytic activity towards the oxidation of ascorbic acid. Our results indicated that among the various metal complexes synthesised, only the Cu(II) complexes were found to be good catalysts towards oxidation of ascorbic acid. It was therefore found interesting to understand the mechanism of oxidation of ascorbic acid in the presence of these copper complexes. For this purpose, one of the Cu(II) complexes has been chosen as the catalyst and a detailed kinetic study of the oxidation of ascorbic acid in methanol-water mixtures was carried out. The results of these studies are presented here.

Materials and Methods

The Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of the following Schiff bases were used for the present study : (i) quinoxaline-2-carboxalidene-2-aminophenol (QAP), (ii) quinoxaline-2-carboxaldehydesemicarbazone (QSC), (iii) quinoxaline-2-carboxalidene-2-furfurylamine(QFA) and (iv) quinoxaline-2-carboxalidene-*o*-phenylene- diamine (QOD).

The synthesis and characterisation of the metal complexes are reported elsewhere[12]. All the solutions of the catalysts (1.0×10^{-4} mol dm^{-3}) were prepared in methanol afresh before each kinetic run. A 1.0×10^{-3} mol dm^{-3} solution of l-ascorbic acid (BDH, Analar) was prepared in water afresh before each kinetic run. A 1:1 mixture of methanol and water was used as the solvent for the reaction mixtures. Analytical reagent grade methanol was used through out the study. All other reagents used were of analytical grade purity. Triply distilled water was used throughout the study.

A Shimadzu UV-Vis 160A spectrophotometer with 1 cm quartz cells was used for absorbance measurements.

All kinetic runs were carried out at 28 ± 0.1 °C. Requisite amounts of all the reagents except ascorbic acid were taken in a reaction bottle. The reaction was initiated by transferring the calculated amount of ascorbic acid into the reaction bottle and

Table 1 — Initial rates obtained in the screening studies of catalytic activity of the complexes on the oxidation of ascorbic acid.

[Ascorbic acid] = 1.0×10^{-4} mol dm^{-3}; [catalyst] = 1.0×10^{-6} mol dm^{-3}

Catalyst	Rate of conversion ($dm^3 mol^{-1} s^{-1}$) x 10^9
—	2.29
$[Mn(QAP)_2]$	3.69
$[Fe(QAP)_2Cl]$	3.80
$[Co(QAP)_2]$	13.3
[Ni(QAP)2]	7.27
$[Cu(QAP)_2]$	103.15
$[Mn(QSC)Cl_2]$	1.45
$[Fe(QSC)Cl_3]$	8.03
$[Co(QSC)Cl_2]$	2.14
$[Ni(QSC)Cl_2]$	23
$[Cu(QSC)Cl_2]$	1050
$[Mn(QFA)_2Cl_2]$	3.56
$[Fe(QFA)(OH)_2Cl_2]$	5.08
$[Co(QFA)_2Cl_2]$	0.59
$[Ni(QFA)_2Cl_2]$	1.4
$[Cu(QFA)Cl_2]$	549.73
$[Mn(QOD)Cl_2]$	2.22
$[Fe(QOD)Cl_3]$	315.98
$[Co(QOD)Cl_2]$	6.68
$[Ni(QOD)Cl_2]$	3.19
$[Cu(QOD)Cl_2]$	444.01

monitored by following the absorbance of ascorbic acid at 265 nm, where it has maximum absorbance and all other substances present in the reaction mixture have negligible absorbance. The concentration of ascorbic acid was obtained from the absorbance data using a molar absorption coefficient of 7500 at 265 nm.

The initial rates of the reaction were obtained by fitting the concentration versus time data into a polynomial of the form,

$$c = a_1 + a_2 t + a_3 t^2 + \ldots$$

and obtaining the slope of the curve[13] at $t = 0$. A software called "axum" (Trimetrix, 1989) was used for this purpose. All the kinetic results were found to be reproducible within an error of 5 %.

Results and Discussion

Screening studies

The results of the catalytic activity of the synthesised complexes are given in Table 1. The data indicate that among the various metal complexes synthesised all the complexes of copper(II) were found to show significant catalytic activity in the oxidation of ascorbic acid to dehydroascorbic acid and none of the manganese(II) complexes were catalytically active. Next to the copper complexes, iron(III) complex of the ligand QOD has the maximum activity. Apart from these complexes, QAP complexes of cobalt(II) and nickel(II), QFA complex of iron(III), QSC complexes of nickel(II) and iron(III) and QOD complex of cobalt(II) also have a slight catalytic activity. Among all the copper(II) complexes, the complex of the ligand QSC was found to be the most active catalyst.

Ascorbic acid is found to be oxidized by several iron(III) and copper(II) chelates. In most of these studies the rate was found to be independent of the partial pressure of oxygen and dissociative mechanism was assumed. Hence it was proposed that the stability of the metal chelates and the steric factors related to the orientation and dimensions of the ligand donor groups can affect the rate[6].

The present investigation indicated that in spite of the considerable variation in the structure and stability, all the copper complexes were found to be active, while in the case of the other complexes, the slight activity observed had no regular dependence on either the nature of the ligand or the structure of the complexes as a whole. Thus it can be inferred that the catalytic activity of the synthesised complexes of the Schiff bases derived from quinoxaline-2-carboxaldehyde is highly influenced by the nature of the metal ion involved. But it is not clear whether dissociative type of mechanism is operative in these reactions also and therefore it is proposed to make a detailed kinetic study in order to obtain an insight into the mechanism.

Kinetic study of the oxidation of ascorbic acid in the presence of the copper complex of quinoxaline-2-carboxalidene-2-aminophenol

The initial rate data obtained in the present kinetic investigation on the catalytic oxidation of ascorbic acid to dehydroascorbic acid is presented in Table 2.

In the present reaction, the order in catalyst is unity as evidenced by a linear plot of initial rate versus [complex], passing through the origin.

When the kinetic runs were carried out in the presence of varying amounts of ascorbic acid in

Table 2- Effect of varying the concentration of the catalyst and added ligand and the dielectric constant of the medium on the initial rate

[ascorbic acid] = 1.0×10^{-4} mol dm^{-3}

[catalyst] $\times 10^6$ (mol dm^{-3})	[ligand] $\times 10^6$ (mol dm^{-3})	Solvent dielectric constant (D)	Initial rate $\times 10^8$ ($dm^3 mol^{-1} s^{-1}$)
1.0	0.0	55.58	2.2
2.0	0.0	55.58	5.0
6.0	0.0	55.58	15.0
10.0	0.0	55.58	25.3
1.0	0.0	55.58	2.7
1.0	1.0	55.58	2.2
1.0	6.0	55.58	1.9
1.0	8.0	55.58	1.7
1.0	10.0	55.58	1.5
2.0	0.0	60.17	2.2
2.0	0.0	57.89	3.3
2.0	0.0	53.29	6.5
2.0	0.0	50.99	13.6

the range 2.0 - 20.0 x 10^{-5} mol dm^{-3}, at a constant catalyst concentration of 1.0 x 10^{-6} mol dm^{-3} in 1:1 methanol water mixtures, the initial rate of the reaction is found to remain constant within the limits of experimental error. It can therefore be inferred that the reaction is zero order with respect to ascorbic acid. The initial rate of the reaction decreases with increase in added ligand concentration (Table 2). A plot of reciprocal of the initial rate versus [ligand] is found to be linear with an intercept on the rate axis.

To study the effect of polarity of the solvent on the rate, kinetic runs were carried out, varying the composition of the solvent. The dielectric constant (D) of the solvent is calculated assuming linear relationship of dielectric constant with composition. A plot of $1/D$ versus log(initial rate) (Table 2) is found to be linear with negative slope. From this plot it can be inferred that, the undissociated acid is the reactive species in this reaction.

In order to study the self decomposition of the complex, reaction was carried out in the absence of ascorbic acid, in 1:1 methanol-water mixtures employing the concentration of the complex as 1.0 x 10^{-5} mol dm^{-3}. The reaction was initiated by transferring the catalyst solution into the solvent and was monitored by following the absorbance of the complex at 235 nm. From this study, the initial rate of self decomposition of the complex was determined to be 3.5×10^{-10} mol dm^{-3}.

The zero order dependence of the initial rate of the reaction on [ascorbic acid] gives the impression that the mechanism of the reaction involves the oxidation of the catalyst by molecular oxygen in a slow step, followed by a fast step in which ascorbic acid is oxidised. If this is the mechanism of the reaction the rate determining step should be independent of [ascorbic acid]. In that case the rate of the reaction should be equal to the rate of oxidation of the complex in the absence of ascorbic acid. However, when the rate of decomposition of the complex was monitored in the absence of ascorbic acid, even at the highest concentration of the complex that has been employed in the catalysed reaction, the rate of decomposition of the complex was much less than that of the oxidation of ascorbic acid. Therefore, in order to explain the observed zero order dependence of initial rate with respect to ascorbic acid, the formation of an intermediate between the complex and ascorbic acid which further reacts with molecular oxygen has been presumed. Further, the observed ligand effect indicates that either the catalyst exists as an equilibrium mixture of two species, as may be expressed by the following equation

$$ML_2 \leftrightarrow ML + L$$

where ML_2 is the undissociated complex and ML is the monodissociated species, or due to the ligand being liberated during the formation of the intermediate between the complex and ascorbic acid.

On the basis of the observed results, the mechanism of the reaction in the first case may be assumed to be the one given by Eqs(1-4).

$$Cu(II)L_2 \overset{K}{\leftrightarrow} Cu(II)L + L \quad \ldots(1)$$

$$Cu(II)L + AA \overset{K_1}{\leftrightarrow} Cu(II)L(AA) \quad \ldots(2)$$

$$Cu(II)L(AA) \xrightarrow[\text{slow}]{k} DHA + Cu(I)L \quad \ldots(3)$$

$$Cu(I)L + O_2 \xrightarrow[\text{fast}]{} Cu(II)L \quad \ldots(4)$$

where $Cu(II)L_2$ represents the undissociated complex, and Cu(II)L is the monodissociated

species, AA and DHA represent ascorbic acid and dehydroascorbic acid respectively, and the species formed by the interaction of AA with Cu(II)L is represented by Cu(II)L(AA). Cu(I)L is the reduced form of the species Cu(II)L and it is oxidised back to Cu(II)L by molecular oxygen.

This mechanism leads to the rate Eq.(5)

$$\text{Rate} = kKK_1[\text{cat}]_t[\text{AA}]_e/\{K+[\text{L}]\}\{1+K_1[\text{AA}]_e\} \quad ...(5)$$

where $[\text{cat}]_t$ represents the total concentration of all the species of the catalyst and [L] that of the ligand.

If $1 << K_1[\text{AA}]_e$, Eq (5) reduces to, Eq (6)

$$\text{Rate} = kK[\text{cat}]_t/\{K+[\text{L}]\} \quad ...(6)$$

If $K << [\text{L}]$, Eq (6) reduces to Eq (7)

$$\text{Rate} = kK[\text{cat}]_t/[\text{L}]. \quad ...(7)$$

Since [L] represents the total concentration of the ligand present in the solution, it includes the concentration of the ligand formed from equilibrium1 as well as the concentration of the ligand added. If we represent the former as $[\text{L}]_i$ and the latter as $[\text{L}]_a$, we obtain the rate equation as

$$\text{Rate} = kK[\text{cat}]_t/\{[\text{L}]_i+[\text{L}]_a\} \quad ...(8)$$

Rearranging Eq (8)

$$1/\text{Rate} = \{[\text{L}]_i/kK[\text{cat}]_t\} + \{[\text{L}]_a/kK[\text{cat}]_t\} \quad ...(9)$$

Equation (9) indicates that a plot of 1/(initial rate) versus $[\text{L}]_a$ should be linear with an intercept on the rate axis, provided $[\text{L}]_i$ is a constant.

Considering the other case, if the observed ligand effect is due to the liberation of the ligand during the formation of the intermediate between the catalyst and ascorbic acid, then the mechanism of the reaction may be represented as given by eqs (10) and (11).

$$\text{Cu(II)L}_2 + \text{AA} \xrightarrow{K'} \text{Cu(II) L(AA)} + \text{L} \quad ...(10)$$

$$\text{Cu(II)L(AA)} \xrightarrow[\text{slow}]{k'} \text{Cu(I)L} + \text{DHA} \quad ...(11)$$

Cu(I)L is then oxidised by molecular oxygen to give Cu(II)L in a fast step.

This mechanism leads to the rate expression,

$$\text{Rate}=k'K'[\text{Cu(II)}]_t[\text{L}]_e[\text{AA}]_e/\{[\text{L}]_e+K'[\text{AA}]_e\} \quad ...(12)$$

where $[\text{Cu(II)}]_t$ is the total concentration of all the species of Cu(II) in solution.

Assuming $[\text{AA}]_e$ is equal to the total concentration of ascorbic acid [AA], from Eq(12) we get,

$$\text{Rate} = k'K'[\text{Cu(II)}]_t[\text{L}]_e[\text{AA}]/\{[\text{L}]_e+K'[\text{AA}]\} \quad ...(13)$$

If $K'[\text{AA}]>>[\text{L}]_e$ then Eq (13) reduces to Eq (14)

$$\text{Rate} = k'[\text{Cu(II)}]_t \quad ...(14)$$

This may be the case in the absence of added ligand. But probably when the ligand is added $[\text{L}]_e$ is no longer negligible compared to K'[AA]. Under such conditions if it is assumed that the concentration of the ligand at equilibrium $[\text{L}]_e$ is equal to the concentration of the ligand added [L], Eq (13) becomes, Eq (15).

$$\text{Rate} = k'K'[\text{Cu(II)}]_t[\text{AA}]/\{[\text{L}]+K'[\text{AA}]\} \quad ...(15)$$

which can be rearranged as Eq (16)

$$1/\text{Rate} = [\text{L}]/\{(k'K'[\text{Cu(II)}]_t[\text{AA}]) + (1/k'[\text{Cu(II)}]_t)\} \quad ...(16)$$

Equation (16) indicates that at constant [AA] and the [catalyst]; (1/rate) versus [L] should be linear with an intercept on the rate axis, as has been observed.

Thus both the proposed mechanisms can explain all the kinetic results obtained. In both the proposed mechanisms, the rate determining step involves dissociation of the intermediate species formed between the catalyst and ascorbic acid.

Acknowledgment

S.M. is thankful to UGC, New Delhi, for the award of a research fellowship and N.S. is thankful to CSIR, New Delhi, for the award of RA.

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