

## Copper(II) complexes of (salicylidene)amino acid schiff bases as models: Peroxidase and catalase

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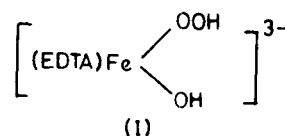
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Activity of copper(II) complexes of (salicylidene)amino acid schiff bases have been tested towards the decomposition of hydrogen peroxide at 40°C and over a wide range of pH 6.0-11.0. Detailed kinetic investigations for the disproportionation of hydrogen peroxide catalysed by the complexes of the general formula,  $\text{Cu}[(\text{sal:aa})\text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$  (where sal:aa = salicylideneamino acid schiff base derived from the condensation of salicylaldehyde and glycine/L-valine/L-methionine;  $n = 0$  or 2) at 40°C and at pH 9.0 are discussed. The decomposition of hydrogen peroxide catalysed by the above complexes conforms to Michaelis-Menten type kinetics.

Metal ions as such or their complexes have been shown to possess enzyme like activity. Peroxidase and catalase are the most extensively studied enzymes and created a lot of interest in the synthesis of model compounds. The metal ion catalyzed disproportionation of  $\text{H}_2\text{O}_2$  has received much attention; this is mainly stimulated by the natural occurrence of a heme-iron enzyme, i.e., catalase, which enhances the decomposition dramatically<sup>1</sup>. Reaction 1 is also catalyzed by Cu(II) complexes<sup>2-4</sup>, provided the coordination sphere is accessible for  $\text{H}_2\text{O}_2$  and/or  $\text{HOO}^-$ .



Sigel *et al.*<sup>3</sup> studied the catalytic action of copper(II)-ethylenediamine complex on the decomposition of hydrogen peroxide, and proposed a binuclear model as an intermediate complex. Copper complexes with amino acids, amines, diamines, di- and tripeptides, biuret, heterocyclic compounds, some proteins<sup>5,6</sup>, 2,2'-bipyridyl, bis(2,9-dimethyl-1,10-phenanthroline)<sup>4,7-11</sup>, and imidazole<sup>12</sup> have been found to show very high catalytic activity towards decomposition of hydrogen peroxide. Iron(III) complexes with EDTA have also been used as catalysts by Walling *et al.*<sup>13</sup> in which they have assigned  $[\text{Fe}^{\text{III}}\text{EDTA}]^{3-}\text{O}_2$  as an active species responsible for the decomposition of hydrogen peroxide. Recently similar work has been carried out by Francis *et al.*<sup>14</sup> to explore other possibilities of the active intermediates and suggested six-coordinated complex (I) as an active intermediate. Reports on the use of the metal schiff base complexes as catalyst towards the decomposition of hydrogen peroxide are scanty.



Recently, Oishi *et al.*<sup>15</sup> have studied the catalytic effect of some planar schiff base complexes of copper(II) and pointed out that the binuclear Cu(II) complexes are more active than the mononuclear complexes.

In continuation of our previous studies on the evolution of iron containing enzymes<sup>16-18</sup> we report herein the kinetic studies on decomposition of hydrogen peroxide catalysed by copper(II) schiff base complexes of the general formula,  $[\text{Cu}(\text{sal:aa})\text{H}_2\text{O}] \cdot n\text{H}_2\text{O}$  [where  $n = 0$  or 2, sal:aa = schiff bases derived from the condensation of salicylaldehyde and glycine/L-valine/L-methionine].

### Materials and Methods

L-Methionine (Fluka), glycine, L-valine, salicylaldehyde, hydrogen peroxide and copper acetate monohydrate (all BDH) were used as supplied and were of AnalaR grade. All other chemicals and solvents (BDH) were of reagent grade.

*Preparation of*  $[\text{Cu}(\text{sal:gly})\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Cu}(\text{sal:L-valine})\text{H}_2\text{O}]$  and  $[\text{Cu}(\text{sal:L-methionine})\text{H}_2\text{O}]$

N-salicylideneglycinatoaquocopper(II) dihydrate and N-salicylidene-L-methioninatoaquocopper(II) were prepared by the methods of Ueki *et al.*<sup>19</sup> and

Table 1—Analytical data and magnetic moment (B.M.) of [Cu(sal:aa)H<sub>2</sub>O]·nH<sub>2</sub>O

| Complex*<br>(empirical formula)                                                                        | Colour     | m.p.<br>(°C) | Yield<br>(%) | Elemental analysis % obs. (calc.) |                |                |                  | Magnetic<br>moment<br>(B.M.) |
|--------------------------------------------------------------------------------------------------------|------------|--------------|--------------|-----------------------------------|----------------|----------------|------------------|------------------------------|
|                                                                                                        |            |              |              | Cu                                | N              | H              | C                |                              |
| [Cu(sal:gly)H <sub>2</sub> O]·2H <sub>2</sub> O<br>(C <sub>9</sub> H <sub>13</sub> O <sub>6</sub> NCu) | Green      | > 300        | 80           | 21.55<br>(21.50)                  | 4.52<br>(4.75) | 4.38<br>(4.41) | 36.51<br>(36.66) | 1.9                          |
| [Cu(sal:L-val)H <sub>2</sub> O]<br>(C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> NCu)                | Dark green | > 300        | 70           | 21.11<br>(21.14)                  | 4.70<br>(4.66) | 4.85<br>(4.99) | 47.65<br>(47.91) | 1.7                          |
| [Cu(sal:L-meth)H <sub>2</sub> O]<br>(C <sub>12</sub> H <sub>15</sub> O <sub>4</sub> NSCu)              | Dark green | > 300        | 75           | 19.09<br>(19.10)                  | 4.20<br>(4.21) | 4.48<br>(4.51) | 43.40<br>(43.29) | 2.1                          |

\*sal:gly = salicylidene-glycine, sal:L-val = salicylidene-L-valine, sal:L-meth = salicylidene-L-methionine.

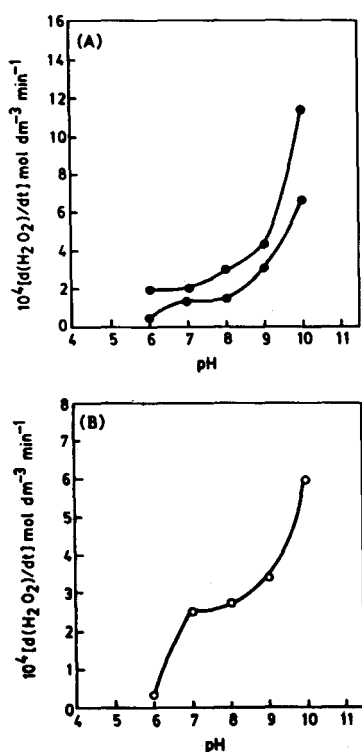


Fig. 1—Hydrogen peroxide decomposition rate as a function of pH. [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> = 2.0 × 10<sup>-2</sup> M; [Catalyst] = 1.0 × 10<sup>-4</sup> M; temp. = 40 ± 0.1°C (A : ● [Cu(sal:gly)H<sub>2</sub>O]·2H<sub>2</sub>O, ○ [Cu(sal:L-meth)H<sub>2</sub>O], B : ○ [Cu(sal:L-val)H<sub>2</sub>O])

Ramanujam *et al.*<sup>20</sup>, respectively. N-salicylidene-L-valinatoaquocopper(II) was also similarly prepared. The complexes were prepared by reacting the pre-formed schiff base *in situ* with copper(II) acetate monohydrate. The appropriate amino acid (0.01 mol) was dissolved in minimum amount of water and an aqueous ethanolic solution (25 ml) of salicylaldehyde (0.01 mol) was added. The mixture was heated over a water bath to about 50°C for 1 hr. To this solution, an aqueous saturated solution of copper(II) acetate monohydrate (0.01 mol) was added

with constant stirring, and then refluxed for 30 min. The solid product was filtered, washed with water, ethanol and finally with ether, and dried over P<sub>4</sub>O<sub>10</sub> in a vacuum desiccator.

The complexes were characterized by elemental analyses, vibrational and electronic spectral and magnetic studies. Carbon, hydrogen and nitrogen in the complexes were determined on CHN rapid analyzer at IIT, New Delhi. Copper was determined by using atomic absorption spectrometer IL-751. Elemental analysis data of the complexes are in good agreement with the reported values and are presented in Table 1.

The infrared spectra of the complexes were recorded in KBr disc on FTIR (4000–450 cm<sup>-1</sup>). The spectra of the complexes show a broad band centred around 3410 cm<sup>-1</sup>, indicating a coordinated water molecule, which was also supported by thermogravimetric analysis. The weight loss corresponding to one mole of water in the complexes took place above 150°C, showing clearly that water was coordinated to the metal. A strong clearly splitted band in the region 1660–1600 cm<sup>-1</sup> had been assigned to the asymmetric carboxyl stretching and the symmetric carboxylate group stretching (ν<sub>s</sub>COO), respectively<sup>20</sup>. Bands at 950 ± 15 and 754 ± 8 cm<sup>-1</sup> might be attributed to the rocking and wagging modes of the coordinated water<sup>21,22</sup>. The νCu–N and the νCu–O had also been assigned at 542 ± 10 and 482 ± 15 cm<sup>-1</sup>, (ref. 21), respectively.

Magnetic moments of the complexes (Table 1) measured at room temperature using vibrating sample magnetometer model-155 were in the range 1.7–2.1 B.M., suggesting the presence of one unpaired electron per copper atom<sup>20</sup>.

The electronic absorption spectra of the com-

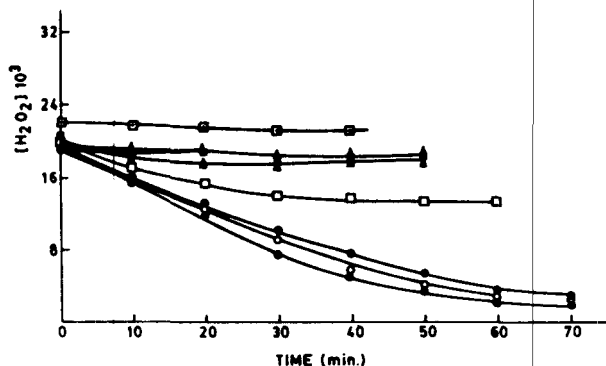


Fig. 2— $[Cu(sal:aa)H_2O] \cdot nH_2O$  catalyzed decomposition of Hydrogen peroxide at  $pH=9.0$ ;  $[H_2O_2] = 2.0 \times 10^{-2} M$ ;  $[Catalyst] = 1.0 \times 10^{-4} M$ ;  $temp. = 40 \pm 0.1^\circ C$  [ $\square$  Without Catalyst,  $\bullet$   $[Cu(sal:gly)H_2O] \cdot 2H_2O$ ,  $\circ$   $[Cu(sal:L-meth)H_2O]$ ,  $\square$   $[Cu(sal:L-val)H_2O]$ ]; [ $\square$  With  $Cu^{2+}$  ion,  $\Delta$  (sal:gly),  $\blacksquare$  (sal:L-meth),  $\blacktriangle$  (sal:L-val)]

plexes in methanol were recorded on a Unicam Sp. 500 spectrophotometer. The copper(II) complexes exhibited two low energy bands at  $\approx 15,000$  and  $\approx 26,250 \text{ cm}^{-1}$  which were assigned as  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions, respectively<sup>20</sup>. The high intensity of the second band was probably due to intensity stealing from the adjacent charge transfer band. In addition to this, the spectra of the complexes exhibited bands in the regions  $40,320$ – $40,240$  and  $36,720$ – $36,560 \text{ cm}^{-1}$  which might be due to the  $\pi$ – $\pi^*$  transition of the benzenoid and  $n$ – $\pi^*$  COO and  $\pi$ – $\pi^*$  transition of  $(C=N)$  chromophore of the ligand, respectively<sup>23</sup>.

From spectral studies it was evident that the ligands, N-salicylideneamino acids (schiff bases) functioned as tridentate ligands with ONO donor sets. The three functional groups along with one molecule of water occupy the planar positions around copper(II). In view of the presence of a coordinated water molecule in the present set of complexes and the observed normal magnetic moments for copper(II), the most probable structure was the one similar to N-salicylidene-glycinato-aquo-copper(II) dihydrate wherein the carboxyl oxygen of a second molecule was coordinated to the metal of the first molecule leading to a square pyramidal arrangement<sup>19</sup>.

#### Rate measurements: Decomposition of $H_2O_2$

Test for catalytic activity of Cu(II) complexes of schiff bases derived from amino acids for decomposition of hydrogen peroxide was initiated by adding known amount of catalyst (1 ml of  $0.0025 M$  solution in alcohol) into hydrogen peroxide solution (25 ml of  $0.01$ – $0.12 M$ ) previously thermostated at  $40^\circ C$ . After regular interval samples were taken out of the

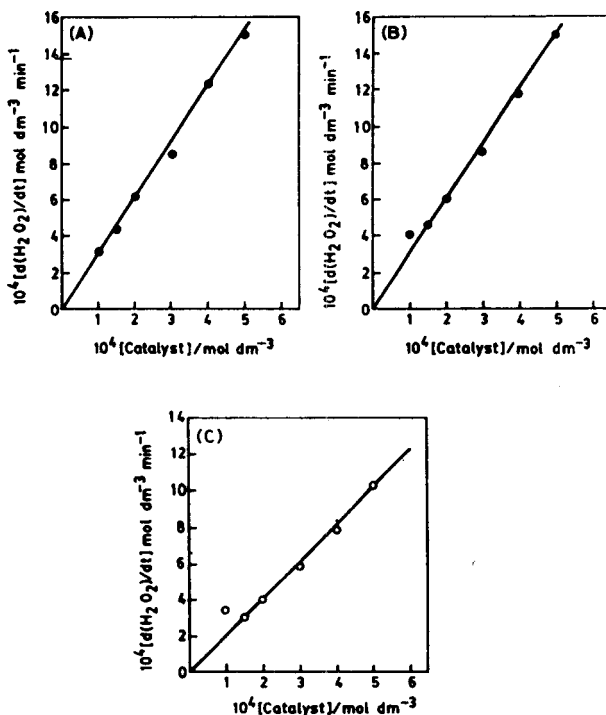


Fig. 3—Hydrogen peroxide decomposition rate as a function of  $[Catalyst]$ ;  $[H_2O_2]_0 = 2.0 \times 10^{-2} M$ ;  $pH=9.0$ ;  $temp. = 40 \pm 1^\circ C$  (A :  $\bullet$   $[Cu(sal:gly)H_2O] \cdot 2H_2O$ , B :  $\circ$   $[Cu(sal:L-meth)H_2O]$ , C :  $\circ$   $[Cu(sal:L-val)H_2O]$ )

reaction solutions and mixed with titanium sulphate in  $1.5 M H_2SO_4$ , and the absorption at  $420 \text{ nm}$  was read from a Beckman Du-6 spectrophotometer.

The data for  $[H_2O_2]$  at corresponding time did not fit a simple rate equation, therefore the initial rate method was used to determine the order of reaction with respect to hydrogen peroxide and catalyst.

#### Results and Discussion

The stability of the complexes have been checked in various buffers ( $pH$  6.0–11.0). No change is observed in the electronic spectra of the complexes in buffers even after 24 hr, which indicates that the complexes are not dissociated in the buffers used.

First of all, the dependence of  $pH$  (6.0–11.0) for the catalysis of the decomposition of  $H_2O_2$  has been investigated at a fixed initial  $[H_2O_2]$  ( $2 \times 10^{-2} M$ ) and a constant  $[catalyst]$  ( $1 \times 10^{-4} M$ ). Dependency of decomposition rate on  $pH$  of the reaction mixture is shown in Fig. 1. An increase in decomposition rate with increase in  $pH$  may be due to participation of  $\bar{O}H$  and  $\bar{O}OH$  species, rather than undissociated hydrogen peroxide molecule. A value of  $pH$  9.0 was found to be most suitable for carrying out all kinetic studies. In alkaline medium  $HO_2^-$  species has been proposed by Francis *et al.*<sup>14</sup> to be the most effective

Table 2—Kinetic constants for decomposition of hydrogen peroxide catalyzed by [Cu(sal:aa)H<sub>2</sub>O]·nH<sub>2</sub>O  
[Catalyst] = 1.0 × 10<sup>-4</sup> M, pH = 9.00, temp. = 40°C

| Complex                                         | $V'_{\max}$<br>(M min <sup>-1</sup> ) <sup>a</sup> | Turnover number<br>(M) <sup>b</sup> | $K'_M$<br>(min <sup>-1</sup> ) <sup>c</sup> |
|-------------------------------------------------|----------------------------------------------------|-------------------------------------|---------------------------------------------|
| [Cu(sal:gly)H <sub>2</sub> O]·2H <sub>2</sub> O | 0.54 × 10 <sup>-2</sup>                            | 54.54                               | 0.4237                                      |
| [Cu(sal:L-val)H <sub>2</sub> O]                 | 1.21 × 10 <sup>-2</sup>                            | 121.21                              | 0.7075                                      |
| [Cu(sal:L-meth)H <sub>2</sub> O]                | 1.51 × 10 <sup>-2</sup>                            | 151.51                              | 0.6025                                      |

a,  $V'_{\max} = \frac{k_1 k_5 [\text{Cu}]_T}{k_1 + k_5 [\text{H}^+]/K_w}$ ; b, Turnover number =  $V'_{\max}/[\text{Cu}]_T$ ; c,  $K'_M = K_M [\text{H}^+]/K_{\text{H}_2\text{O}_2}$

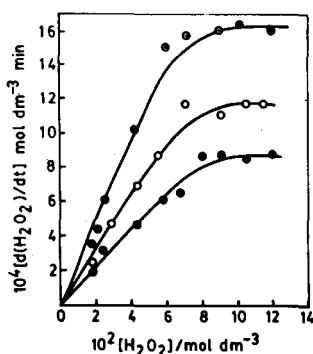
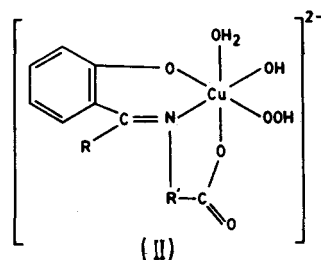


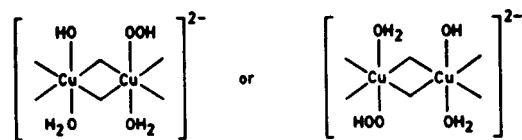
Fig. 4—Hydrogen peroxide decomposition rate as a function of [H<sub>2</sub>O<sub>2</sub>] at pH = 9.0; [Catalyst] = 1 × 10<sup>-4</sup> M; temp. = 40 ± 1°C (● [Cu(sal:gly)H<sub>2</sub>O]·2H<sub>2</sub>O, ○ [Cu(sal:L-meth)H<sub>2</sub>O], ○ [Cu(sal:L-val)H<sub>2</sub>O])

species around pH range 9.0–11.0 which easily could form a complex of the type (I) and decomposition of this complex makes the rate determining step for [Fe(III)EDTA]<sup>-</sup> catalyzed decomposition of hydrogen peroxide. In our experiments probability of formation of a hexa-coordinated complex like [Cu(sal:aa)H<sub>2</sub>O(OH)(OOH)]<sup>2-</sup> is possible because the most probable structure for the catalyst, [Cu(sal:aa)H<sub>2</sub>O]·nH<sub>2</sub>O is one wherein the carboxyl oxygen of a second molecule is weakly coordinated to the metal of first molecule leading to a square pyramidal arrangement. It is, therefore, thought that initially  $\bar{\text{O}}\text{H}$  is coordinated to metal by replacing weakly-bonded carboxyl oxygen of a second molecule and subsequently  $\text{H}\bar{\text{O}}_2$  coordinates in the sixth available coordination site leading to the octahedral Cu(II) complex of the type [Cu(sal:aa)H<sub>2</sub>O(OH)(OOH)]<sup>2-</sup> (II) as an active intermediate.

Sigel<sup>2</sup> compared the catalase like activities of a number of copper(II) chelates and pointed out that copper polyamine chelate with two free coordination sites show maximum activity while fully coordinated copper(II) complex is inactive. A high catalytic activity was observed for decomposition of H<sub>2</sub>O<sub>2</sub> by Mn(II) and Fe(III) chelates of diethyltriarnine



when two coordination sites in metal ion were available for inner sphere mechanism as proposed by Wang and Jarinagin<sup>24,25</sup>. In our experiments, the possibility of outer sphere mechanism was completely discarded and inner sphere mechanism with two available coordination sites for  $\bar{\text{O}}\text{H}$  and  $\bar{\text{O}}\text{OH}$  species is, therefore, probably responsible for activity of these Cu(II) complexes for decomposition of hydrogen peroxide. Other possibilities for the intermediate could not be ignored in which  $\bar{\text{O}}\text{H}$  and  $\bar{\text{O}}\text{OH}$  coordinate to the copper atoms in the binuclear non-planar (square pyramidal) structure of the catalyst as given below,

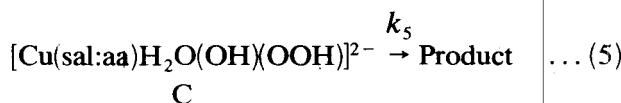
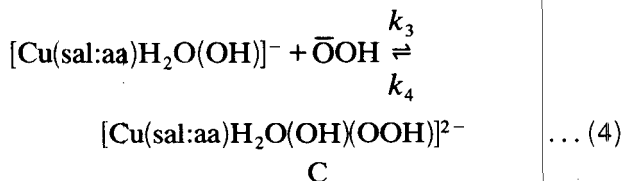
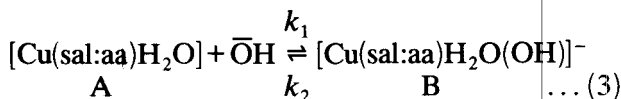


where one electron transfer between  $\bar{\text{O}}\text{OH}$  and copper atom is assumed to proceed in the inner-sphere mechanism.

In order to ensure that the catalytic activity observed in decomposition of hydrogen peroxide was only due to N-salicylideneaminoacetic acidcopper(II) derivatives and not because of traces of uncomplexed metal ions, 10% solution of 2,2'-bipyridyl was added. Addition of 2,2'-bipyridyl, however, did not change the rate of catalytic activity. Addition of ligands as catalyst was also not effective (Fig. 2).

A tentative mechanism for decomposition of hydrogen peroxide catalysed by N-salicylideneamino-

acidaquocopper(II) complexes may be written as in Scheme 1.



Scheme 1

The proposed mechanism is somewhat similar to the mechanism proposed by Sigel *et al.*<sup>4</sup> for decomposition of hydrogen peroxide catalysed by  $\text{Cu}^{2+}$  ions and Cu(II) complexes of 2,2'-bipyridyl. Applying steady state approximation of B and C species, the rate of decomposition of hydrogen peroxide may be written as in Eq. (6).

$$v = -\frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{k_1 k_5 K_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] [\text{Cu}]_{\text{T}}}{k_1 K_{\text{M}} [\text{H}^+] + K_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] \left( k_1 + \frac{k_5 [\text{H}^+]}{K_{\text{w}}} \right)} \quad \dots (6)$$

Also rearranging Eq. 6 in Lineweaver-Burk form of equation:

$$\frac{1}{v} = \frac{K_{\text{M}} [\text{H}^+]}{k_5 K_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] [\text{Cu}]_{\text{T}}} + \frac{k_1 + \left[ \frac{k_5 [\text{H}^+]}{K_{\text{w}}} \right]}{k_1 k_5 [\text{Cu}]_{\text{T}}} \quad \dots (7)$$

$$\text{where, } K_{\text{M}} = \frac{k_4 + k_5}{k_3}$$

Equation 6 clearly indicates that decomposition of  $\text{H}_2\text{O}_2$  follows a first order kinetics with respect to [catalyst], which is in accord with our experimental findings (Fig. 3). The initial rate as function of  $[\text{H}_2\text{O}_2]$  is shown in Fig. 4, where linearity of the curve at lower  $[\text{H}_2\text{O}_2]$  suggests first order dependency at lower  $[\text{H}_2\text{O}_2]$ , whereas at higher concentration the reaction rate becomes constant showing inde-

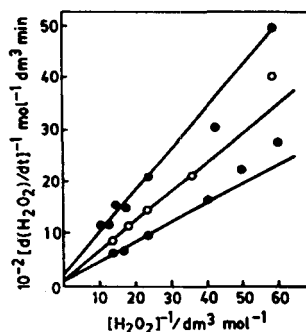


Fig. 5—Lineweaver-Burk plot (●  $[\text{Cu}(\text{sal:gly})\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$ , ○  $[\text{Cu}(\text{sal:L-meth})\text{H}_2\text{O}]$ , ◻  $[\text{Cu}(\text{sal:L-val})\text{H}_2\text{O}]$ )

pendency on  $[\text{H}_2\text{O}_2]$ . The independency of decomposition of hydrogen peroxide at higher  $[\text{H}_2\text{O}_2]$  could also be explained from Eq. 6 due to the presence of  $[\text{H}_2\text{O}_2]$  term in denominator. The most exciting feature of Eq. 5 lies in its nature, being a typical Michaelis-Menten type of kinetics supported by the linear plot (Fig. 5),  $(d[\text{H}_2\text{O}_2]/dt)^{-1}$  versus  $[\text{H}_2\text{O}_2]^{-1}$ . Intercept and slope obtained in Fig. 5 should be equal to

$$\frac{k_1 + \left[ \frac{k_5 [\text{H}^+]}{K_{\text{w}}} \right]}{[k_1 k_5 [\text{Cu}]_{\text{T}}]} \quad \text{and} \quad \frac{[K_{\text{M}} [\text{H}^+]]}{[k_5 K_{\text{H}_2\text{O}_2} [\text{Cu}]_{\text{T}}]}$$

respectively, as warranted by Eq. 7. On comparing the terms with normal Michaelis-Menten curve,

$$\text{Intercept} = \frac{1}{V'_{\text{max}}}$$

$$\text{where, } \frac{1}{V'_{\text{max}}} = \frac{k_1 + k_5 [\text{H}^+]/K_{\text{w}}}{k_1 k_5 [\text{Cu}]_{\text{T}}}$$

$$\text{and slope} = \frac{K'_{\text{M}}}{k_5 [\text{Cu}]_{\text{T}}}$$

$$\text{where, } K'_{\text{M}} = \frac{K_{\text{M}} [\text{H}^+]}{K_{\text{H}_2\text{O}_2}}$$

From the intercept and slope,  $V'_{\text{max}}$  and  $K'_{\text{M}}$  and turnover numbers have been calculated and are tabulated in Table 2. All three complexes show almost similar activity towards disproportionation of  $\text{H}_2\text{O}_2$  which indicates that the structural factor is most important in the catalytic function of copper(II) complexes. Although greater activity of  $[\text{Cu}(\text{sal:L-meth})\text{H}_2\text{O}]$  than  $[\text{Cu}(\text{sal:L-val})\text{H}_2\text{O}]$  is due to the fact that methionine group weakens the bonding between the carboxyl oxygen of second molecule and the copper atom of the first molecule in the structure of the catalyst, thereby, producing more easily available site for incoming  $\bar{\text{O}}\text{H}/\bar{\text{O}}\text{OH}$  groups. On

the other hand, small size of the glycine is most probably responsible for less activity of [Cu(sal:gly)-H<sub>2</sub>O]·2H<sub>2</sub>O than [Cu(sal:L-val)-H<sub>2</sub>O].

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