On the Kinetics and Mechanism of the Reactions of Hydrogen Peroxide with Hydrazine or Hydroxylamine, Catalyzed by Cu^{2+} and by the Cu^{2+}–2,2′-Bipyridyl Complex[1,2]

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Abstract: The peroxidase-like reaction between H_2O_2 and NH_2NH_2 is catalyzed by Cu^{2+} as by the Cu^{2+}–2,2′-bipyridyl 1:1 complex. The kinetics of this reaction were investigated by measuring the initial velocity, v_0, of the decreasing concentration of H_2O_2 (25°). The results found in the presence of Cu^{2+}–bipyridyl can be summarized in the equation $v_0 = -d[H_2O_2]/dt = k[Cu(bipy)][H_2O_2][NH_2NH_3^+]/[H^+]$. The investigations in the presence of only Cu^{2+} are complicated by precipitation, but it is still certain that $v_0 \sim [H^+]^{-1}$ and $v_0 \sim [Cu^{2+}]$. These results give evidence that the reaction mechanism is similar with both catalysts. A mechanism which is in accord with the above-mentioned kinetic equation is postulated and discussed as is the structure and the subsequent reactions of the active complex. Also the peroxidase-like reaction between H_2O_2 and NH_2OH is catalyzed both by Cu^{2+} and by the Cu^{2+}–2,2′-bipyridyl 1:1 complex. The kinetics of these reactions were investigated too by measuring the initial velocity, v_0, of the decreasing concentration of H_2O_2 (25°). For the investigations in the presence of Cu^{2+}–2,2′-bipyridyl, v_0 was found to be proportional to $[H^+]^{-1}$, $[H_2O_2]$, and [Cu(bipy)], yet the dependence of v_0 from $[NH_2OH]$ is not clear. The results found in the presence of Cu^{2+} can be summarized in the equation $v_0 = -d[H_2O_2]/dt = k[Cu^{2+}][H_2O_2][NH_3OH^+]/[H^+]$. A mechanism with structure and subsequent reactions of the active complex is postulated and discussed. A comparison is made between the catalase-like decomposition of H_2O_2 and the peroxydase-like reactions between H_2O_2 and NH_2NH_2 or NH_2OH. The peroxidase-like reaction between H_2O_2 and NH_2NH_2 in the presence of the Cu^{2+}–2,2′-bipyridyl 1:1 complex, also as between H_2O_2 and NH_2OH when catalyzed by Cu^{2+}, seems to go over pathways similar to the catalase-like decomposition of H_2O_2 in the presence of the Cu^{2+}–2,2′-bipyridyl 1:1 complex.

In the preceding communication,[2] the catalase-like activity of the Cu^{2+}–2,2′-bipyridyl 1:1 complex was investigated. Based on the results obtained from a study of the kinetics involved, a mechanism for the decomposition of H_2O_2 in the presence of the mentioned catalyst was proposed. Since it is known that the peroxidase-like reaction (1) between the isosteric molecules, H_2O_2 and NH_2NH_2, is catalyzed by metal ions and their

$$2H_2O_2 + NH_2NH_2 \longrightarrow N_2 + 4H_2O \qquad (1)$$

respective complexes,[4] it seemed to be of interest to investigate the kinetics of this system also in the presence of the Cu^{2+}–2,2′-bipyridyl 1:1 complex so as to be able to compare the mechanism of a catalase-like and a peroxidase-like system.

Reaction 1 is also catalyzed by the hydrated Cu^{2+} ion;[5] therefore, we included this catalyst in the investigations. However, it became obvious that this system could be investigated only in a restricted manner, since precipitates were formed.

Besides reaction 1, the Cu^{2+}–bipyridyl 1:1 complex, like the "free" Cu^{2+} ion, catalyzes the reaction between H_2O_2 and the isosteric NH_2OH.[5] In this case, probably N_2 is a preponderant product, but eventually N_2O, NO_2^-, and NO_3^- also arise.[6-9] Though it is not quite clear yet which the products are, we also included in this study an investigation of the kinetics of the reaction between H_2O_2 and NH_2OH with Cu^{2+} and the Cu^{2+}–2,2′-bipyridyl complex as catalysts.

Experimental Section

$NH_2NH_2 \cdot H_2O$ and $NH_2OH \cdot HCl$ were obtained from Merck AG, Darmstadt, Germany. The origin of the remaining reagents is as given before.[2]

The experiments were performed as described previously.[2] Again the initial rate of the decreasing concentration of H_2O_2 was measured as $v_0 = -d[H_2O_2]/dt$ (mole $l.^{-1}$ min^{-1}).

Results and Discussion

The Cu^{2+}–2,2′-Bipyridyl–NH_2NH_2–H_2O_2 System. Firstly, the catalysis of reaction 1 was investigated with respect to dependence on pH (5–7) at constant initial concentrations of H_2O_2 and NH_2NH_2 with constant Cu^{2+} and 2,2′-bipyridyl (bipy) concentrations (*cf.* Figure 1a). For the initial velocity of the decreasing concentration of H_2O_2, it was found that v_0 is proportional to $[H^+]^{-1}$.

The dependence of the reaction velocity of the initial concentration of H_2O_2 was investigated at different pH values, where the initial concentration of H_2O_2 was varied from 2×10^{-3} to 3.2×10^{-2} *M* (Figure 1a). From the dependence between log v_0 and log $[H_2O_2]$ at constant pH (Figure 1b), a linear proportionality was found between v_0 and $[H_2O_2]$.

In the same manner, the dependence of the initial

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(1) Part XXI in the series Metal Ions and H_2O_2.

(2) Part XX: H. Sigel, C. Flierl, and R. Griesser, *J. Amer. Chem. Soc.*, **91**, 1061 (1969).

(3) Correspondence should be addressed to this author.

(4) F. A. Cotton and G. Wilkinson, "Anorganische Chemie," Verlag Chemie, Weinheim/Bergstrasse, Germany, 1967, p 313.

(5) H. Erlenmeyer, C. Flierl, and H. Sigel, *Chimia* (Aarau), **22**, 433 (1968).

(6) "Gmelins Handbuch der Anorganischen Chemie," System-Nr. 3, "Sauerstoff," Lieferung 7, Verlag Chemie, Weinheim/Bergstrasse, 1966, p 2293; *cf.* also System-Nr. 23, "Ammonium," 1936, p 572.

(7) C. P. Lloyd and W. F. Pickering, *J. Inorg. Nucl. Chem.*, **29**, 1907 (1967).

(8) N. Hlasivcová, J. Novák, and J. Zýka, *Collect. Czech. Chem. Commun.*, **32**, 4403, 4410 (1967).

(9) J. H. Anderson, *Analyst*, **91**, 532 (1966); **89**, 357 (1964).

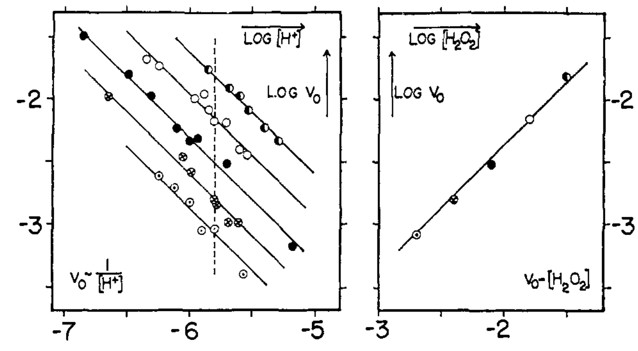

Figure 1. (a) Peroxidase-like activity (reaction 1) of the Cu^{2+}–2,2′-bipyridyl-NH_2NH_2–H_2O_2 system ($[Cu^{2+}]_{tot} = [bipy]_{tot} = 4 \times 10^{-4}$ *M*) at a constant initial concentration of $NH_2NH_3^+$ (8×10^{-3} *M*) but different initial concentrations of H_2O_2 (◐, 3.2×10^{-2} *M*; ○, 1.6×10^{-2} *M*; ●, 8×10^{-3} *M*; ⊗, 4×10^{-3} *M*; ⊙, 2×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 1a at pH 5.8.

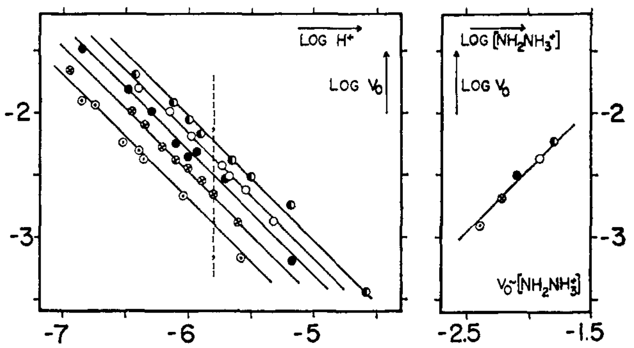

Figure 2. (a) Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2NH_2–H_2O_2 system ($[Cu^{2+}]_{tot} = [bipy]_{tot} = 4 \times 10^{-4}$ *M*) at a constant initial concentration of H_2O_2 (8×10^{-3} *M*), but different initial concentrations of $NH_2NH_3^+$ (◐, 1.6×10^{-2} *M*; ○, 1.2×10^{-2} *M*; ●, 8×10^{-3} *M*; ⊗, 6×10^{-3} *M*; ⊙, 4×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 2a at pH 5.8.

velocity on the initial concentration of NH_2NH_2 was determined, where the concentration was varied from 4×10^{-3} to 1.6×10^{-2} *M* (Figure 2a). The concentration range investigated could not be enlarged, since Cu_2O precipitates with too much NH_2NH_2 (*cf.* ref 10), and at too little concentration of NH_2NH_2 the points of measurement were shifted in the pH range in which a disproportion of H_2O_2 might occur.[5,11] For the concentration range mentioned, one gets the results illustrated in Figure 2b, since NH_2NH_2 is protonated ($pK^H_{NH_2NH_3} = 8.07$; *cf.* ref 5) under the conditions of investigation, and hence it follows that v_0 is proportional to $[NH_2NH_3^+]$.

In another range investigated, v_0 was determined as a function of the concentration of the catalyst; the concentrations $[Cu^{2+}]_{tot} = [bipy]_{tot}$ were varied from 10^{-4} to 8×10^{-4} *M* (Figure 3a). From the data in Figure 3b, one sees that v_0 is proportional to [Cu(bipy)].

In a fourth set of measurements, the proportion between Cu^{2+} and 2,2′-bipyridyl was varied. The maximum catalytic activity again was found, as expected (*cf.* ref 2), at a concentration ratio of 1:1 (Figure 4); *i.e.*, the Cu^{2+}–2,2′-bipyridyl 1:1 complex, under the conditions of measurements where it is formed in a nearly quantitative manner, has to be considered as the effective catalyst.

The kinetic results obtained can be summarized in eq 2, where for the initial velocity of the decreasing concentration of H_2O_2 it holds that

$$v_0 = -\frac{d[H_2O_2]}{dt} = k\frac{[Cu(bipy)][H_2O_2][NH_2NH_3^+]}{[H^+]} \qquad (2)$$

From the experimental results, one can calculate that the velocity constant, *k*, for eq 2 is 2.05×10^{-1} (mole^{-1}/l. min^{-1}). Since the stability constants of the different Cu^{2+}–2,2′-bipyridyl complexes are known,[12] the concentrations of these can be calculated for the different excesses of bipyridyl given in Figure 4. The initial velocity can then be calculated with the aid of eq 2. The values for log $v_{0,calcd}$ in Table I agree well with the experimental ones (log $v_{0,exptl}$) if the excess of bipyridyl is not too large and therefore the measurements are not carried out at too high pH values. With large excesses of bipyridyl, the experiments have to be carried out in a pH range where the hydrolysis and complexing with HOO^- play an essential part (*cf.* ref 2), and thus log $v_{0,exptl}$ and log $v_{0,calcd}$ no longer agree. These problems, together with the assumption that $[Cu(bipy)_2]^{2+}$ is an ineffective catalyst,[13] have been discussed in more detail in the preceding paper.[2]

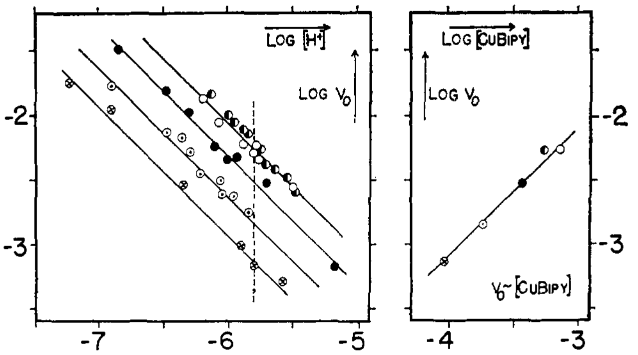

Figure 3. (a) Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl-NH_2NH_2–H_2O_2 system at constant initial concentrations of H_2O_2 and $NH_2NH_3^+$ (8×10^{-3} *M* each) but different equivalent concentrations of Cu^{2+} and bipyridyl ($[Cu^{2+}]_{tot} = [bipy]_{tot}$: ○, 8×10^{-4} *M*; ◐, 6×10^{-4} *M*; ●, 4×10^{-4} *M*; ⊙, 2×10^{-4} *M*; ⊗, 10^{-4} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 3a at pH 5.8. The concentrations of the Cu^{2+}–2,2′-bipyridyl 1:1 complex were calculated with the aid of the constants given by Irving and Mellor[12] and the total concentrations given in Figure 3a.

The kinetic results summarized in eq 2 can be ex-

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(10) T. R. Bhat, D. Radhamma, and J. Shankar, *J. Inorg. Nucl. Chem.*, 27, 2641 (1965).

(11) That NH_2NH_2 really is consumed during the reaction was proved through titration with $KMnO_4$ and the aid of a calibration curve, since the reaction between NH_2NH_2 and $KMnO_4$ is not stoichiometric.

(12) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962).

(13) This already can be seen from the calculated results in Table I for $[Cu^{2+}] = 4 \times 10^{-4}$ *M* and $[bipy] = 6 \times 10^{-4}$ and 8×10^{-4} *M*. Though in both cases considerable amounts of $[Cu(bipy)_2]^{2+}$ are formed, *i.e.*, 1.94×10^{-4} and 3.35×10^{-4} *M*, the values log $v_{0,calcd}$ agree quite well with log $v_{0,exptl}$, the latter values calculated for $[Cu(bipy)^{2+}] = 2.04 \times 10^{-4}$ and 4.46×10^{-5} *M*.

Table I. Comparison of the Logarithms of the Initial Velocities of the Decreasing Concentration of H_2O_2 Experimentally Found (Log $v_{0,\text{exptl}}$) at pH 5.8 and at Different 2,2′-Bipyridyl Excesses, Corresponding with Figure 4, with the Calculated Ones (Log $v_{0,\text{calcd}}$)

$[\text{bipy}]_{\text{tot}}$[a]	$[Cu^{2+}]$[b]	$[Cu(bipy)]$[b]	$[Cu(bipy)_2]$[b]	$[Cu(bipy)_3]$[b]	Log $v_{0,\text{exptl}}$	Log $v_{0,\text{calcd}}$
4×10^{-4}	1.83×10^{-5}	3.64×10^{-4}	1.81×10^{-5}	7.16×10^{-9}	−2.52	...
6×10^{-4}	5.37×10^{-7}	2.04×10^{-4}	1.94×10^{-4}	1.47×10^{-6}	−2.88	−2.77
8×10^{-4}	1.49×10^{-8}	4.46×10^{-5}	3.35×10^{-4}	2.00×10^{-5}	−3.36	−3.43
1.6×10^{-3}	1.47×10^{-11}	9.96×10^{-7}	1.70×10^{-4}	2.29×10^{-4}	−3.76	−5.08

[a] In all cases, $[Cu^{2+}]_{\text{tot}} = 4 \times 10^{-4}$ *M;* $[H_2O_2]_{\text{tot}} = [NH_2NH_2]_{\text{tot}} = 8 \times 10^{-3}$ *M; cf.* Figure 4. [b] Calculated with the aid of the constants given in ref 12.

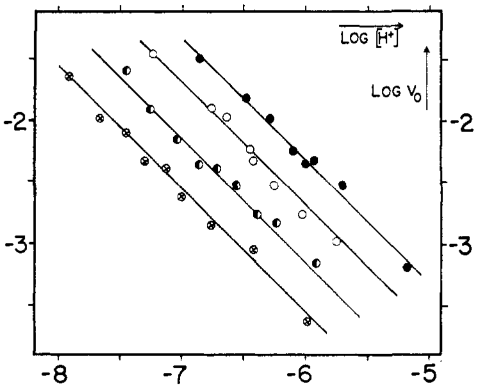


Figure 4. Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2NH_2–H_2O_2 system at constant initial concentrations of H_2O_2 and $NH_2NH_3^+$ (8×10^{-3} *M* each) and a constant Cu^{2+} concentration (4×10^{-4} *M*) but different concentrations of 2,2′-bipyridyl (●, 4×10^{-4} *M;* ○, 6×10^{-4} *M;* ◐, 8×10^{-4} *M;* ⊗, 1.6×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°).

plained through the reaction mechanism given in eq 3–7,

$$NH_2NH_3^+ \overset{K_1}{\rightleftharpoons} NH_2NH_2 + H^+ \tag{3}$$

$$[Cu(bipy)]^{2+} + NH_2NH_2 \overset{K_2}{\rightleftharpoons} [Cu(bipy)(NH_2NH_2)]^{2+} \tag{4}$$

$$[Cu(bipy)(NH_2NH_2)]^{2+} + H_2O_2 \overset{K_3}{\rightleftharpoons} [Cu(bipy)(NH_2NH_2)(H_2O_2)]^{2+} \tag{5}$$

$$[Cu(bipy)(NH_2NH_2)(H_2O_2)]^{2+} \xrightarrow{k^*} IP + \text{products} \tag{6}$$

$$IP + H_2O_2 + (\text{products}) \longrightarrow [Cu(bipy)]^{2+} + N_2 + 4H_2O \tag{7}$$

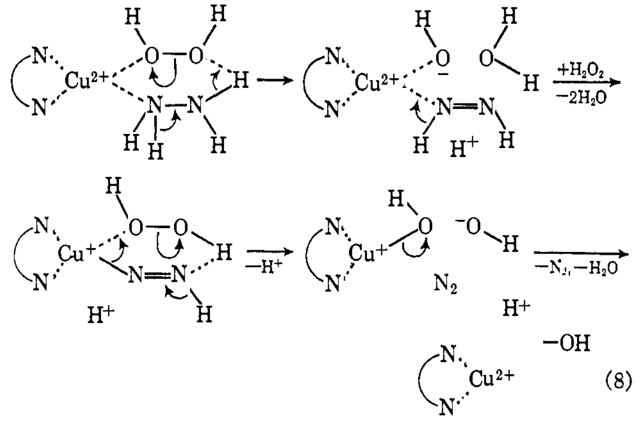
IP = intermediate products

if one assumes that equilibria 3, 4, and 5 favor greater concentrations of reactants on the left side of the equations.

For equilibrium 3, this assumption is true, since the acidity constant, $K_1 = K^{H}_{NH_2NH_3}$, has the value $10^{-8.07}$ (*cf.* ref 5), and the main part of the measurements were done at pH values lower than 7. That equilibrium 4 under the present conditions of measurements is also essentially on the left side, one can show with the aid of the stability constant estimated earlier[5] (log $K^{Cu(bipy)}_{Cu(bipy)(NH_2NH_2)} \cong 3.5$). If one calculates the concentrations of the ternary complex $[Cu(bipy)(NH_2NH_2)]^{2+}$ from the concentrations given in Figure 2a at pH 5.3, 5.8, and 6.3 and plots their logarithms against the corresponding values of log v_0 from Figure 2a, one obtains Figure 5.

The points in Figure 5 lie, with the exception of a part of the values calculated for pH 6.3, on a straight line with a slope of 1; *i.e.*, the initial velocity is proportional to the concentrations of NH_2NH_2 as $[Cu(bipy)(NH_2NH_2)]^{2+}$. Thus the above-mentioned assumption is fulfilled. The small deviation from the straight line of some points calculated for pH 6.3 derives from the fact that under these conditions up to approximately 40% of the total concentration of $[Cu(bipy)]^{2+}$ exists as $[Cu(bipy)(NH_2NH_2)]^{2+}$, and therefore a strong proportionality between the concentration of NH_2NH_2 and $[Cu(bipy)(NH_2NH_2)]^{2+}$ is no longer true. One may assume with great security that the concentrations of the quaternary complex, $[Cu(bipy)(NH_2NH_2)(H_2O_2)]^{2+}$ (*cf.* also ref 2), are small under the conditions employed.

From the mechanism suggested in eq 3–7, the experimentally found eq 2 can be derived where, instead of *k*, one then has to write $k^*K_1K_2K_3$. The structure of the possible active complex and a speculation over the ensuing reactions may be formulated in the following scheme (eq 8).



(8)

An interesting result of this investigation is that, with the Cu^{2+}–2,2′-bipyridyl 1:1 complex as a catalyst, the peroxidase-like reaction (1) between H_2O_2 and NH_2NH_2 occurs in a way similar to the catalase-like reaction, *i.e.*, the disproportionation of H_2O_2 (*cf.* ref 2). In the catalase-like reaction, the initial velocity is proportional to the square of the concentration of H_2O_2 ($v_0 \sim [H_2O_2]^2$), and in the peroxidase-like reaction, to the product, $[H_2O_2][NH_2NH_3^+]$. This points to a close relationship of both reactions. Similar reaction mechanisms with similar active complexes and their following reactions can be postulated for both cases (*cf.* eq 8 and ref 2).

The Cu^{2+}–NH_2NH_2–H_2O_2 System. For comparison an attempt was made to investigate reaction 1 with

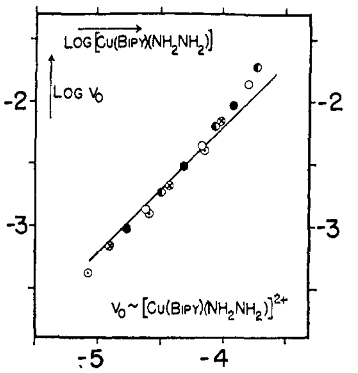


Figure 5. Dependence of the initial velocity, v_0, of the decreasing concentration of H_2O_2 on the concentration of the $[Cu(bipy)(NH_2NH_2)]^{2+}$ complex. Concentrations of the complex were calculated at pH 5.3, 5.8, and 6.3 with the aid of the constants given in an earlier report[5] and the total concentrations given in Figure 2a.

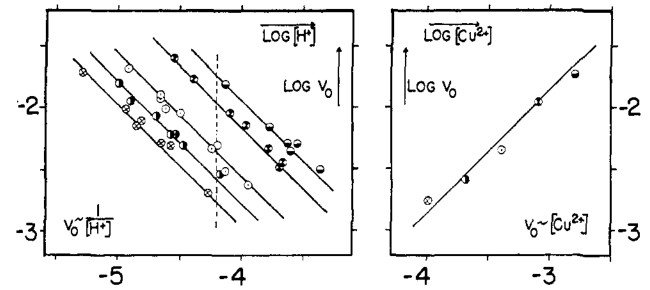


Figure 6. (a) Peroxidase-like activity (reaction 1) of the Cu^{2+}–NH_2NH_2–H_2O_2 system at constant initial concentrations of H_2O_2 and $NH_2NH_3^+$ (1.6 × 10^{-2} M each) but different concentrations of Cu^{2+} ($[Cu^{2+}]_{tot}$: ◓, 1.6 × 10^{-3} M; ◑, 8 × 10^{-4} M; ⊙, 4 × 10^{-4} M; ◐, 2 × 10^{-4} M; ⊗, 10^{-4} M) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 6a at pH 4.2.

Cu^{2+} as a catalyst, *i.e.*, without the presence of a carrier ligand. However, the experiments were rendered more difficult since precipitation occurred (*cf.* ref 5). Only the following could be ascertained with security.

The initial velocity of the decreasing concentration of H_2O_2 is inversely proportional to the concentration of hydrogen ion ($v_0 \sim [H^+]^{-1}$; Figure 6a) and directly proportional to the concentration of Cu^{2+} ($v_0 \sim [Cu^{2+}]$; Figure 6b). The dependence of the initial velocity on the initial concentrations of H_2O_2 and NH_2NH_2 could not be determined exactly.[11] However, the results mentioned suggest that reaction 1 occurs in the presence of Cu^{2+} in a way similar to what it does in the presence of the Cu^{2+}–2,2′-bipyridyl 1 : 1 complex.

The Cu^{2+}–2,2′-Bipyridyl–NH_2OH–H_2O_2 System. The investigation of the pH dependence (4.5–6.5) of the peroxidase-like reaction between H_2O_2 and NH_2OH at constant initial concentrations of H_2O_2 and NH_2OH and at constant concentrations of Cu^{2+} equal to 2,2′-bipyridyl (*cf.* Figure 7a) shows that the dependence of the initial velocity on pH is proportional to $[H^+]^{-1}$.

The dependence of the reaction velocity on the initial concentration of H_2O_2 was determined in experiments in which the initial concentration of H_2O_2 was varied from 2 × 10^{-3} to 2.2 × 10^{-2} M (Figure 7a). The results show that v_0 is directly proportional to $[H_2O_2]$ (*cf.* Figure 7b).

Similar experiments (Figure 8a), in which the initial concentrations of NH_2OH were varied from 4 × 10^{-3} to 6.4 × 10^{-2} M, give evidence that the initial velocity is independent from the concentration of NH_2OH (Figure 8b).[14]

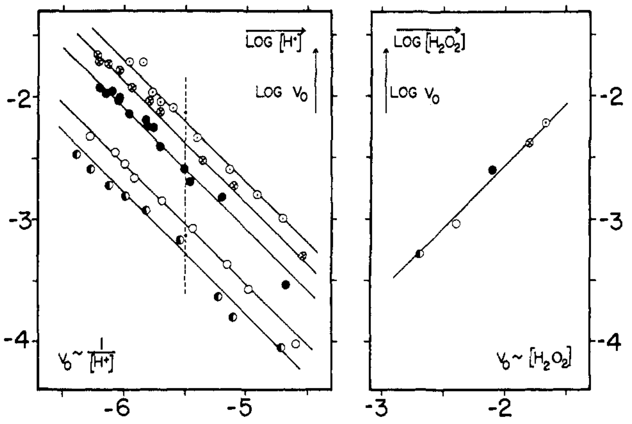


Figure 7. (a) Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2OH–H_2O_2 system ($[Cu^{2+}]_{tot}$ = $[bipy]_{tot}$ = 4 × 10^{-4} M) at a constant initial concentration of NH_2OH (8 × 10^{-3} M) but at different initial concentrations of H_2O_2 (⊙, 2.2 × 10^{-2} M; ⊗, 1.6 × 10^{-2} M; ●, 8 × 10^{-3} M; ○, 4 × 10^{-3} M; ◐, 2 × 10^{-3} M) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 7a at pH 5.5.

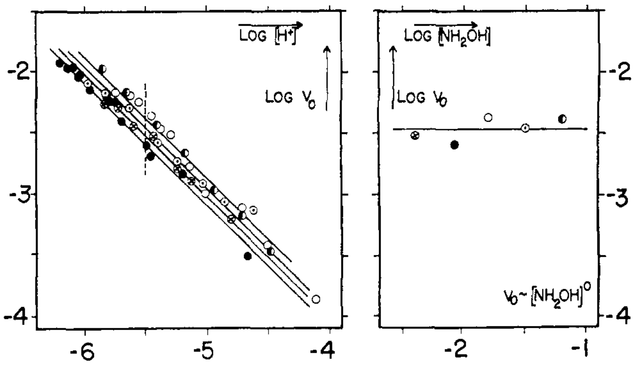


Figure 8. (a) Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2OH–H_2O_2 system ($[Cu^{2+}]_{tot}$ = $[bipy]_{tot}$ = 4 × 10^{-4} M) at a constant initial concentration of H_2O_2 (8 × 10^{-3} M) but at different initial concentrations of NH_2OH (◐, 6.4 × 10^{-2} M; ⊙, 3.2 × 10^{-2} M; ○, 1.6 × 10^{-2} M; ●, 8 × 10^{-3} M; ⊗, 4 × 10^{-3} M) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 8a at pH 5.5.

Since the initial velocity under the conditions of measurement seems to be independent of the concentration of NH_2OH, a scheme for the reaction mechanism has to be advanced either on the supposition that equilibrium 9 is completely on the right side, or that

$$[Cu(bipy)]^{2+} + NH_2OH \rightleftharpoons [Cu(bipy)(NH_2OH)]^{2+} \qquad (9)$$

NH_2OH is involved in the reaction only after the velocity-determining step. If one calculates, with the aid of the acidity constant ($pK^{H}_{NH_3OH}$ = 5.97) and the stability constant ($\log K^{Cu(bipy)}_{Cu(bipy)(NH_2OH)}$ = 2.2) of

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(14) That NH_2OH is consumed during the reaction was proved through titration with $KMnO_4$; *cf.* K. Bhaskara Rao, *Chemist-Analyst*, 49, 40 (1960).

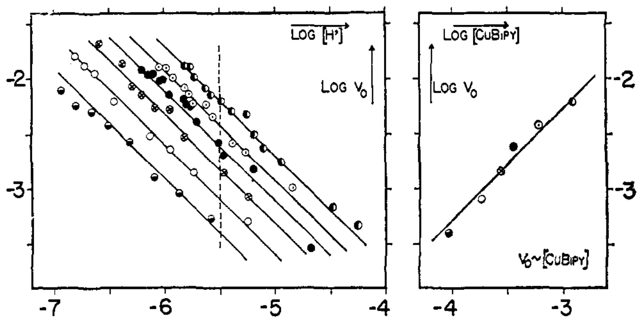

Figure 9. (a) Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2OH–H_2O_2 system at constant initial concentrations of H_2O_2 and NH_2OH (8×10^{-3} *M* each) but at different concentrations of Cu^{2+} and bipyridyl ($[Cu^{2+}]_{tot} = [bipy]_{tot}$: ◐, 1.36×10^{-3} *M*; ⊙, 6.8×10^{-4} *M*; ●, 4×10^{-4} *M*; ⊗, 3×10^{-4} *M*; ○, 2×10^{-4} *M*; ◒, 10^{-4} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 9a at pH 5.5 The concentration of the Cu^{2+}–2,2′-bipyridyl 1:1 complex was calculated with the aid of the constants given by Irving and Mellor[12] and the total concentrations given in Figure 9a.

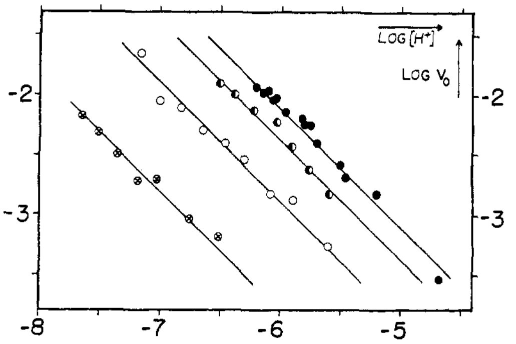

Figure 10. Peroxidase-like activity of the Cu^{2+}–2,2′-bipyridyl–NH_2OH–H_2O_2 system at constant initial concentrations of H_2O_2 and NH_2OH (8×10^{-3} *M* each) and a constant Cu^{2+} concentration (4×10^{-4} *M*) but different concentrations of 2,2′-bipyridyl (●, 4×10^{-4} *M*; ◐, 6×10^{-4} *M*; ○, 8×10^{-4} *M*; ⊗, 1.6×10^{-3} *M*).

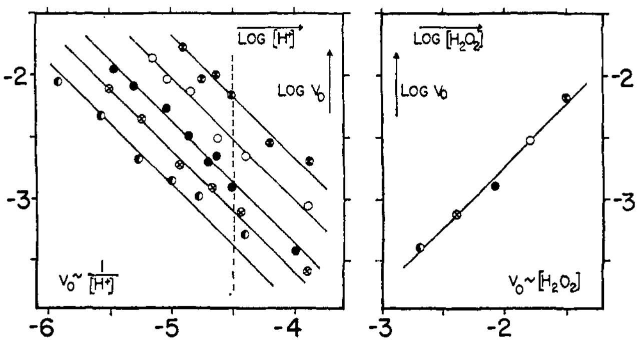

Figure 11. (a) Peroxidase-like activity of the Cu^{2+}–NH_2OH–H_2O_2 system ($[Cu^{2+}] = 4 \times 10^{-4}$ *M*) at a constant initial concentration of NH_3OH^+ (8×10^{-3} *M*) but at different initial concentrations of H_2O_2 (⊛, 3.2×10^{-2} *M*; ○, 1.6×10^{-2} *M*; ●, 8×10^{-3} *M*; ⊗, 4×10^{-3} *M*; ◐, 2×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 11a at pH 4.5.

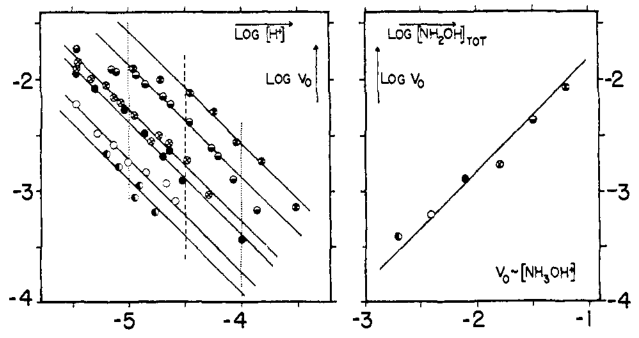

Figure 12. (a) Peroxidase-like activity of the Cu^{2+}–NH_2OH–H_2O_2 system ($[Cu^{2+}] = 4 \times 10^{-4}$ *M*) at constant initial concentrations of H_2O_2 (8×10^{-3} *M*), but at different initial concentrations of NH_3OH^+ (⊛, 6.4×10^{-2} *M*; ◒, 3.2×10^{-2} *M*; ⊗, 1.6×10^{-2} *M*; ●, 8×10^{-3} *M*; ○, 4×10^{-3} *M*; ◐, 2×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 12a at pH 4.5.

equilibrium 9 given previously,[5] the concentrations of the ternary complex $[Cu(bipy)(NH_2OH)]^{2+}$ at pH 5.5, and the concentrations of NH_2OH given in Figure 8a, one finds that the formation of the ternary complex in the investigated range of the concentration of NH_2OH rises from about 14 to near 72%. Hence, this complex is not yet formed in a quantitative manner. On the other hand, this change in the concentration of the ternary complex is about by a factor of 5 which is equivalent to about 0.7 log unit. Therefore, a dependence of the initial velocity of the decreasing concentration of H_2O_2 on the concentration of NH_2OH and on the concentration of the ternary complex should be observable. This consideration therefore suggests on the one hand that NH_2OH is involved in the reaction only after the rate-determining step. On the other hand, a comparison of the rate at low concentrations of H_2O_2 (2×10^{-3} *M*) shows that the rate is about 25 times higher in the presence of 8×10^{-3} *M* NH_2OH (Figure 7a) than in the complete absence of NH_2OH (*cf.* Figure 1 in ref 2). This suggests that the rate is dependent on the concentration of NH_2OH or $[Cu(bipy)(NH_2OH)]^{2+}$. Measurements at lower concentrations of NH_2OH (2×10^{-3} *M*) gave no clear results, since the log v_0 values were scattered. Therefore the dependence of the initial velocity on the concentration of NH_2OH is not yet clear.[15]

In the following series of experiments, v_0 was investigated as a function of the concentration of the catalyst where the concentration $[Cu^{2+}]_{tot} = [bipy]_{tot}$ was varied from 10^{-4} to 1.36×10^{-3} *M* (Figure 9a). The results demonstrate that the initial velocity of the decreasing concentration of H_2O_2 is proportional to the concentration of the Cu^{2+}–2,2′-bipyridyl 1:1 complex (Figure 9b).

In a last series of measurements, the proportion $[Cu^{2+}]_{tot}:[bipy]_{tot}$ was varied from 1:1 to 1:4 (Figure 10). A maximum catalytic activity was found again (*cf.* ref 2) at a ratio of 1:1; *i.e.*, the Cu^{2+}–2,2′-bipyridyl 1:1 complex has to be considered as the effective catalyst. Under the present conditions of investi-

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[15] A possible explanation for this discrepancy is that the concentration of the ternary complex might be greater than the calculations show, and that equilibrium 9 is indeed on the right side.

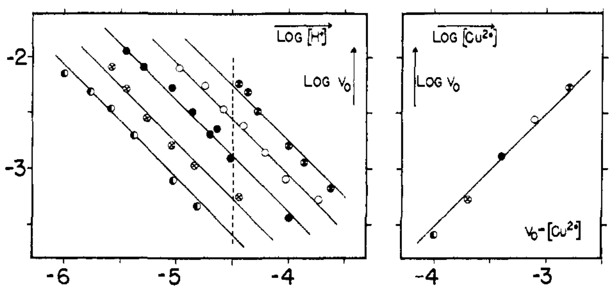

Figure 13. (a) Peroxidase-like activity of the Cu^{2+}-NH_2OH-H_2O_2 system at constant initial concentrations of H_2O_2 and NH_3OH^+ (each 8×10^{-3} *M*) but different concentrations of Cu^{2+} (⊕, 1.6×10^{-3} *M;* ○, 8×10^{-4} *M;* ●, 4×10^{-4} *M;* ⊗, 2×10^{-4} *M;* ◐, 10^{-4} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole $l.^{-1}$ min^{-1}), of the decreasing concentration of H_2O_2 (25°). (b) Evaluation of the results of Figure 13a at pH 4.5.

gation (*cf.*, *e.g.*, Figure 9a), this complex is formed in a practically quantitative manner.

The kinetics results so far obtained for the Cu^{2+}-2,2′-bipyridyl-NH_2OH-H_2O_2 system can be summarized in eq 10; *i.e.*, for the initial velocity of the decreasing concentration of H_2O_2, it holds that

$$v_0 = -\frac{d[H_2O_2]}{dt} = k\frac{[Cu(bipy)][H_2O_2][NH_2OH]?}{[H^+]} \qquad (10)$$

The Cu^{2+}-NH_2OH-H_2O_2 System. If one uses the hydrated Cu^{2+} ion as a catalyst for the reaction between H_2O_2 and NH_2OH, the reaction starts at somewhat lower pH values as in the presence of the carrier ligand 2,2′-bipyridyl (*cf.* ref 5). At higher pH values, precipitation occurs similar to that found in the Cu^{2+}-H_2O_2-NH_2NH_2 system.[5] Nevertheless, in this case the dependence of the initial velocity of the decreasing concentration of H_2O_2 on the concentration of all other reaction compounds could be determined, since the pH range in which one obtains a homogeneous solution is high enough (Figures 11-13).

The investigations were analogous to those with the Cu^{2+}-2,2′-bipyridyl 1:1 complex as a catalyst. It was found that the initial velocity, v_0, of the decreasing concentration of H_2O_2 in the reaction between H_2O_2 and NH_2OH is proportional to $[H^+]^{-1}$ (Figure 11a), $[H_2O_2]$ (Figure 11b), $[NH_2OH^+]$ (Figure 12), and $[Cu^{2+}]$ (Figure 13). These kinetic results can be summarized in the rate equation

$$v_0 = -\frac{d[H_2O_2]}{dt} = k\frac{[Cu^{2+}][H_2O_2][NH_3OH^+]}{[H^+]} \qquad (11)$$

The value of the velocity constant, calculated from the data given in Figure 11, is $k = 1.8$ ($mole^{-1}$ l. min^{-1}). Equation 11 can be derived from the mechanism given in eq 12 through 16, in which $k = k^*K_1K_2K_3$, if one assumes that equilibria 12-14 lie on the left side.

$$NH_3OH^+ \overset{K_1}{\rightleftharpoons} NH_2OH + H^+ \qquad (12)$$

$$Cu^{2+} + NH_2OH \overset{K_2}{\rightleftharpoons} [Cu(NH_2OH)]^{2+} \qquad (13)$$

$$[Cu(NH_2OH)]^{2+} + H_2O_2 \overset{K_3}{\rightleftharpoons} [Cu(NH_2OH)(H_2O_2)]^{2+} \qquad (14)$$

$$[Cu(NH_2OH)(H_2O_2)]^{2+} \xrightarrow{k^*} IP + products \qquad (15)$$

$$IP + NH_2OH + (products) \longrightarrow Cu^{2+} + N_2(?) + 4H_2O \qquad (16)$$

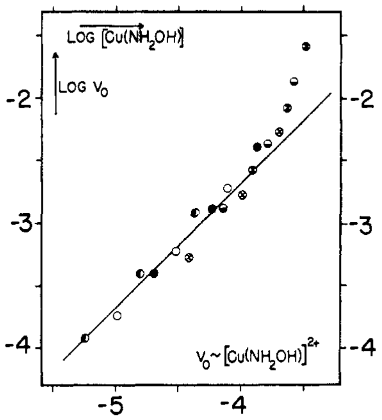

Figure 14. Dependence of the initial velocity of the decreasing concentration of H_2O_2 on the concentration of the Cu^{2+}-NH_2OH complex. The concentration of complex was calculated at pH 4.0, 4.5, and 5.0 with the aid of the constants given previously[5] and the total concentration given in Figure 12a.

As already mentioned for the validity of the postulated reaction mechanism, it is a precondition that the concentrations of the reactants which occur on the right side in equilibria 12-14 are small. This requirement was proved in the following way.

For equilibria 12 and 13, the equilibrium constants are known.[5] For the acidity constant, $K_1 = K^H_{NH_3OH}$, it follows that $pK^H_{NH_3OH} = 5.97$ (*cf.* ref 5); therefore, since the investigations were made in the pH range of 3.5-5.5, equilibrium 12 is actually on the left to a large extent.

The concentrations of the Cu^{2+}-NH_2OH 1:1 complex were calculated for equilibrium 13 with the aid of the stability constant, $K_2 = K^{Cu}_{Cu(NH_2OH)}$ ($\log K^{Cu}_{Cu(NH_2OH)} = 2.8$; *cf.* ref 5), and the acidity constant, $K^H_{NH_3OH}$, for the investigations made with increasing concentration of NH_2OH (Figure 12a) at pH 4.0, 4.5, and 5.0. A plot of the logarithms of these concentrations of the Cu^{2+}-NH_2OH complex against the logarithms of the initial velocity of the decreasing concentration of H_2O_2 (taken from Figure 12a at pH 4.0, 4.5, and 5.0) results in Figure 14.

From the slope of the straight line in Figure 14, the proportionality between the initial velocity and the concentrations of the Cu^{2+}-NH_2OH complex becomes evident: $v_0 \sim [Cu^{2+}$-$NH_2OH]$. The deviation of the points at high concentrations of Cu^{2+}-NH_2OH reflect too "high" log v_0 values. In Figure 12a, at high concentrations of NH_2OH at pH 5.0, an evident flattening of the curves can already be seen; *i.e.*, the values for log v_0 are too large. This explains the deviations in Figure 14 (*cf.* footnote 16).[17]

Based on the above statements about Figure 14, therefore, it is more reasonable to write instead of eq 11

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(16) At the three points in Figure 14, which deviate most from the straight line, about 80, 66, and 57% of the total concentration of Cu^{2+} have formed the Cu^{2+}-NH_2OH complex. For all other points, the concentration of $[Cu(NH_2OH)]^{2+}$, with respect to the total concentration of Cu^{2+}, is between about 1.3 and 49%; *i.e.*, here the proportionality between the concentrations of NH_2OH and Cu^{2+} on one hand and $[Cu(NH_2OH)]^{2+}$ on the other are to a large extent fulfilled.

(17) Cu^{2+}-peroxo complexes could not be proved under the conditions of measurement with the aid of the absorption at 360 nm (*cf.* ref 18); an absorption was found only at higher pH values where precipitation also occurred. Therefore equilibrium 14 is, under the conditions of measurement, on the left side.

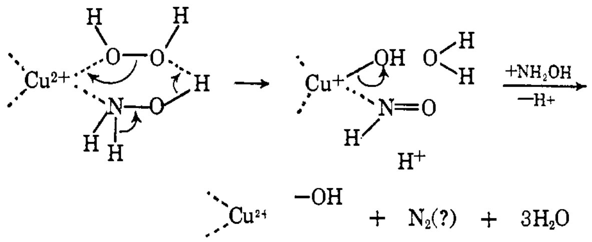
(18) H. Sigel, *Angew. Chem.*, in press.

$$v_0 = -\frac{d[H_2O_2]}{dt} = k'[Cu(NH_2OH)][H_2O_2] = k^*K_3[Cu(NH_2OH)][H_2O_2] \quad (17)$$

Equations 17 and 11 are equivalent with

$$v_0 = -\frac{d[H_2O_2]}{dt} = k^*K^{H}{}_{NH_3OH}K^{Cu}{}_{Cu(NH_2OH)} \times K_3\,\frac{[Cu^{2+}][H_2O_2][NH_3OH^+]}{[H^+]} \quad (18)$$

Also in this case it is possible to postulate an active complex with ensuing reactions (eq 19) similar to the systems of Cu^{2+}–bipyridyl–H_2O_2 (*cf.* ref 2) and Cu^{2+}–bipyridyl–H_2O_2–NH_2NH_2 (eq 8).



(19)

The hypothetical particle, HNO, postulated as an intermediate product in eq 19 was also suggested by Anderson[9] for the alkaline oxidation of NH_2OH by O_2, also with Cu^{2+} as a catalyst. After Anderson,[9] "possibly the hypothetical compound, HNO, is the intermediate from which the nitrous oxide is spontaneously formed, as indicated by the equation"

$$2(HNO) = N_2O + H_2O \quad (20)$$

He also discussed the formation of NO_2^- from HNO. Peroxide then "would oxidize nitrite to nitrate" (*cf.* ref 9).

Conclusions

A comparison of the results from the study of the kinetics of the catalase-like decomposition of H_2O_2 (a) with those of the peroxidase-like reactions, *i.e.*, for systems (b) and (c), makes clear the connection between

H_2O_2/Cu^{2+}–2,2′-bipyridyl 1:1 complex (*cf* ref 2) (a)

$H_2O_2/NH_2NH_2/Cu^{2+}$–2,2′-bipyridyl 1:1 complex (b)

$H_2O_2/NH_2OH/Cu^{2+}$ (c)

the catalase-like and the peroxidase-like reaction. Since similar rate laws for (a) through (c) were found, similar reaction mechanisms with similar active complexes and their subsequent reactions can be postulated. One of the two reacting H_2O_2 molecules in the catalase-like reaction evidently can be replaced by a H donor, *e.g.*, NH_2NH_2. So the Cu^{2+}–2,2′-bipyridyl 1:1 complex is able, depending upon the reaction conditions, to catalyze a catalase-like or peroxidase-like reaction. Consequently this catalyst shows a behavior similar to that known for catalase[19] (*cf.* ref 18). This enzyme too possesses peroxidase-like properties if there are relatively small amounts of H_2O_2 in the reaction milieu which also contains an oxidizable substrate. Similar results were found in a study on the haemin-catalyzed oxidation of ascorbic acid.[20]

The results of our investigations of the peroxidase-like system (c) with Cu^{2+} as a catalyst instead of the Cu^{2+}–2,2′-bipyridyl 1:1 complex suggest that the main function of bipyridyl in these cases is as a carrier.[21] Bipyridyl prevents precipitation at higher pH values (*cf.* ref 2 and 5). For the catalase-like decomposition of H_2O_2, similar experiments cannot be done with Cu^{2+} as a catalyst without a carrier ligand, since precipitation occurs from the beginning.[2,22] The results now in hand for the catalase-like decomposition of H_2O_2 with different Cu^{2+} complexes as catalysts suggest, moreover, that the ligand has some influence on the over-all reaction.[18,22–24]

If the metal ion in reactions a–c herein discussed undergoes a real change of valency, it can be supposed that it occurs between Cu^{I} and Cu^{II}, and not Cu^{III}, since on the one hand Cu^{II} is reduced in an alkaline milieu to yellow copper(I) oxide by NH_2NH_2 (*cf.* ref 10) or by NH_2OH (*cf.* ref 9 and 10), and on the other Cu^{I} again can be oxidized to Cu^{II} by H_2O_2 (*cf.* ref 25). In the formulation of the respective active complexes and their following reactions, this was expressed.

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(19) H. Aebi and A. Hassan, *Helv. Chim. Acta*, 43, 544 (1960).

(20) M. L. Kremer, *Trans. Faraday Soc.*, 63, 1208 (1967).

(21) Besides this, 2,2′-bipyridyl is able to stabilize low oxidation valencies which also may be of some influence; *cf.* ref 4, p 703.

(22) H. Sigel and U. Müller, *Helv. Chim. Acta*, **49**, 671 (1966).

(23) J. Schubert, V. S. Sharma, E. R. White, and L. S. Bergelson, *J. Amer. Chem. Soc.*, **90**, 4476 (1968).

(24) Th. Kaden and H. Sigel, *Helv. Chim. Acta*, **51**, 947 (1968).

(25) A. Zuberbühler, *ibid.*, **50**, 466 (1967).