posed the excess charge density on carbon to be of the order of 0.3 electron, a value somewhat higher than that estimated from the ^{13}C chemical shift.

Several authors have presented correlations of ^{13}C chemical shifts with substituent electronegativity for a series of CH_3X derivatives. Comparison of the methyllithium ^{13}C chemical shifts indicates the electronegativity of lithium in the bridge bonded aggregate to be substantially larger than the Pauling or other values.[21] From a series of CH_3X, where X is a first-row element, a value of 1.5[16] and, from an equation based on a more encompassing series,[5] a value of 1.6 are obtained for the effective electronegativity of lithium (Pauling scale) in the electron-deficient aggregate. By comparison, the Pauling electronegativity of atomic lithium is 1.0. Using the value of $\sim$1.5 for the electronegativity of lithium (and 2.5 for that of carbon), a value of 17% ionic character is calculated[22] for the carbon–lithium bond in methyllithium in ether solution. This contrasts with 35–40% ionic character[23] calculated using the electronegativity of atomic lithium and the 27% ionic character calculated by Ebel.[24]

As reported in Table I, the value of $J_{^{13}C-^{1}H}$ of methyllithium is appreciably smaller than that usually found for sp^3 hybrids.[25] To some extent, the negative charge is indicated to cause small $J_{^{13}C-^{1}H}$ values.[4,26] Presuming the charge is not the only cause of the small $J_{^{13}C-^{1}H}$, the value infers more p character (than in sp^3) to the carbon–hydrogen orbitals, leaving the carbon–lithium orbital high in s character, *i.e.*, $\sim$40%.[27] It seems reasonable that increased s character of this orbital allows better overlap in the composite orbital formed between carbon and the three lithium orbitals. On the other hand, changes in effective nuclear charge can contribute to changes in carbon–proton coupling.[28]

The conclusions regarding the nature of the carbon–lithium bond in methyllithium are expected to be general and relate to other alkyllithium reagents.

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(22) N. B. Hannay and C. P. Smyth, *ibid.*, **68**, 171 (1946).

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(24) H. F. Ebel, *Tetrahedron*, **21**, 699 (1965).

(25) A. W. Douglas, *J. Chem. Phys.*, **45**, 3465 (1966). Other reports of $J_{^{13}C-^{1}H}$ for methyllithium are 98 Hz (T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 5125 (1964)) and 96.5 Hz (H. O. House, W. L. Respess, and G. W. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966)).

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

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Abstract: The decomposition of H_2O_2, catalyzed by the Cu^{2+}–2,2′-bipyridyl system, was investigated by measuring the initial velocity, v_0, of the decreasing concentration of H_2O_2 (25°). The results found can be summarized in the equation $v_0 = -d(H_2O_2)/dt = k[Cu(bipy)][H_2O_2]^2/[H^+]$. A mechanism which is in accord with this equation is discussed as is the structure and the subsequent reactions of the probable active complex. The proposed mechanism can be written without the formulation of *free* radicals.

The systematic investigation of the decomposition of H_2O_2 (eq1), catalyzed by Cu^{2+} complexes as well as

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \tag{1}$$

catalase, showed that Cu^{2+} complexes are catalytically active only if the coordination sphere is not saturated by the ligand.[3] This result gives evidence that ternary Cu^{2+}–peroxo–ligand complexes are involved during the reaction. Indeed these can be demonstrated by spectrophotometric measurements.[3,4]

Investigations of the kinetics of the Cu^{2+}–ethylenediamine–H_2O_2 system showed that in this case the reaction probably goes over a binuclear complex,[5] while in the phosphate-buffered Cu^{2+}–histamine–H_2O_2 system, probably a monomeric complex is involved.[6] To learn more about the mechanism of such a catalysis, we investigated the kinetics of the decomposition of H_2O_2 with the Cu^{2+}–2,2′-bipyridyl system as a catalyst.

Experimental Section

2,2′-Bipyridyl and $Cu(ClO_4)_2 \cdot 6H_2O$ were from Fluka AG, Buchs,

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

(2) Part XIX: H. Erlenmeyer, C. Flierl, and H. Sigel, *Chimia* (Aarau), **22**, 433 (1968).

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

(4) H. Brintzinger and H. Erlenmeyer, *Helv. Chim. Acta*, **48**, 826 (1965).

(5) T. Kaden and H. Sigel, *ibid.*, **51**, 947 (1968).

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

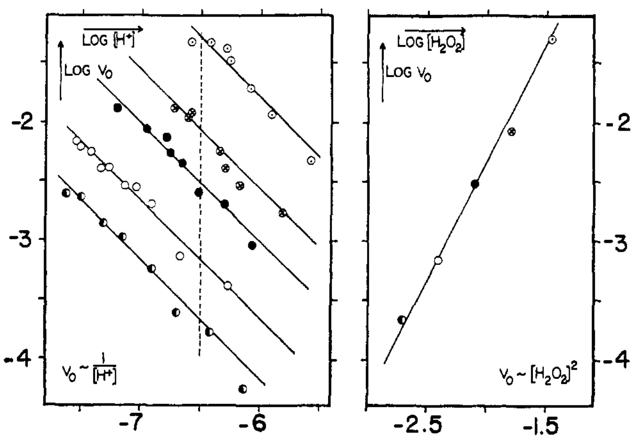

Figure 1. (a) Catalytic activity of the Cu^{2+}–2,2′-bipyridyl system ($[Cu^{2+}]_{tot}$ = $[bipy]_{tot}$ = 4×10^{-4} *M*) at different initial concentrations of H_2O_2 (⊙, 3.2×10^{-2} *M;* ⊗, 1.6×10^{-2} *M;* ●, 8×10^{-3} *M;* ○, 4×10^{-3} *M;* ◐ 2×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decomposition of H_2O_2 (25°). (b) Evaluation of the results of Figure 1a at pH 6.5.

Switzerland. H_2O_2 (pro analysi), $TiOSO_4$, and $KHSO_4$ were obtained from Merck AG, Darmstadt, Germany.

"Standard" reaction solutions (5 ml) contained $[Cu^{2+}]_{tot}$ = [2,2′-bipyridyl]$_{tot}$ = 4×10^{-4} *M* and $[H_2O_2] = 8 \times 10^{-3}$ *M* (25°). Starting from this solution, the concentrations of Cu^{2+}, 2,2′-bipyridyl, or H_2O_2 were varied. Before the addition of H_2O_2, the pH was adjusted a little higher as desired with 2 *N* NaOH. After the addition of H_2O_2, the pH was read from a potentiometer (potentiometer E 353 B and microglass electrode U from Metrohm AG, Herisau, Switzerland). After certain periods, samples were taken out of the reaction solutions and mixed with titanyl sulfate in 1.5 *M* H_2SO_4, and the absorption at 410 nm (ϵ 737 l. mole^{-1} cm^{-1}) was read from a Beckman spectrophotometer B (*cf.* ref 5).

The initial reaction velocity, $v_0 = -d[H_2O_2]/dt$ (mole l.$^{-1}$ min^{-1}), was taken from the slope of the tangent of the H_2O_2 concentration–time curve at the time, $t = 0$. The logarithms of the initial velocities plotted against the logarithms of the varied concentration of X gave a straight line. From the slope of this, the relation between the reaction velocity and the concentration of X was taken.[5,7]

Results

First of all, the dependence on pH (5.5–7.5) for the catalysis of the decomposition of H_2O_2 was investigated at a constant initial H_2O_2 concentration and a constant Cu^{2+} and 2,2′-bipyridyl (bipy) concentration (*cf.* Figure 1a). For the initial rate, results show that v_0 is proportional to $[H^+]^{-1}$.

The reaction velocities at different initial concentrations of H_2O_2 (2×10^{-3}–2.3×10^{-2} *M*) as dependent on pH are shown in Figure 1a. At constant pH (Figure 1b), v_0 is proportional to $[H_2O_2]^2$.

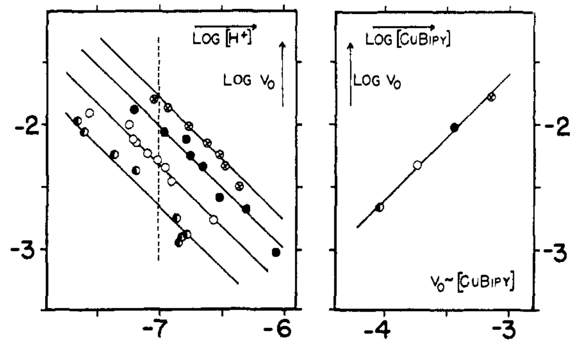

Figure 2. (a) Catalytic activity of the Cu^{2+}–2,2′-bipyridyl system at a constant initial concentration of H_2O_2 (8×10^{-3} *M*) but different concentrations of Cu^{2+} and bipyridyl ($[Cu^{2+}]_{tot}$ = $[bipy]_{tot}$ ⊗, 8×10^{-4} *M;* ●, 4×10^{-4} *M;* ○, 2×10^{-4} *M;* ◐, 10^{-4} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decomposition of H_2O_2 (25°). (b) Evaluation of the results of Figure 2a at pH 7.0. The concentrations of the Cu^{2+}–2,2′-bipyridyl 1:1 complex were calculated with the aid of the constants[9] given by Irving and Mellor[10] and the total concentrations given in Figure 2a.

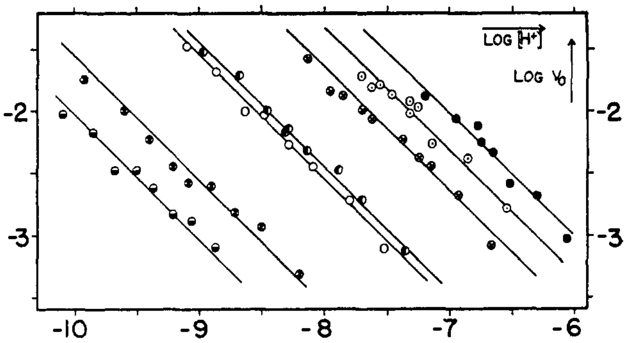

Figure 3. Catalytic activity of the Cu^{2+}–2,2′-bipyridyl system at a constant initial concentration of H_2O_2 (8×10^{-3} *M*) and a constant Cu^{2+} concentration (4×10^{-4} *M*) but different concentrations of 2,2′-bipyridyl (●, 4×10^{-4} *M;* ⊙, 6×10^{-4} *M;* ⊗, 8×10^{-4} *M;* ◐, 10^{-3} *M;* ○, 1.28×10^{-3} *M;* ⨂, 2×10^{-3} *M;* ◒, 4×10^{-3} *M*) in dependence on pH; determined as the initial velocity, v_0 (mole l.$^{-1}$ min^{-1}), of the decomposition of H_2O_2 (25°).

In another series, the concentrations $[Cu^{2+}]_{tot}$ = $[bipy]_{tot}$ were varied from 10^{-4} to 8×10^{-4} *M* (Figure 2a). At these conditions, the Cu^{2+}–2,2′-bipyridyl 1:1 complex is nearly quantitatively formed;[8] however, its exact concentration was calculated with the constants[9] determined by Irving and Mellor.[10] In Figure 2b, the log v_0 values at pH 7 from Figure 2a are plotted against the logarithms of the concentrations of the Cu^{2+}–2,2′-bipyridyl 1:1 complex. These results show that v_0 is proportional to [Cu(bipy)].

Finally the ratio of Cu^{2+}:2,2′-bipyridyl was varied (Figure 3). The maximum catalytic activity was with the proportion 1:1, which suggests that the Cu^{2+}–2,2′-bipyridyl 1:1 complex is the effective catalyst. This result is different from that found in the Cu^{2+}–ethylenediamine–H_2O_2 system,[5] where the greatest catalytic activity was found in the ratio Cu^{2+}:ethylenediamine = 1:1.5.

These results can be summarized in eq 2 for the initial rate of the decomposition of H_2O_2. Since except for the

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

velocity constant, *k*, all values from eq 2 are known, the constant can be calculated for $k = 4.12 \times 10^{-2}$ (mole^{-1} l. min^{-1}). With this value, one can calculate the values of log $v_{0,calcd}$ from the curves of Figure 3, where

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(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953.

(8) Cu^{2+} alone is at these conditions a poor catalyst (*cf.* also ref 6). This was proved with solutions at the above-mentioned concentrations, but without 2,2′-bipyridyl (in this case a precipitate is formed).

(9) $pK^{H}_{H(bipy)} = 4.59$; $\log K^{Cu}_{Cu(bipy)} = 8.10$; $\log K^{Cu(bipy)}_{Cu(bipy)_2} = 5.50$; $\log K^{Cu(bipy)_2}_{Cu(bipy)_3} = 3.40$; *cf.* ref 10.

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

Table I. Comparison of the Logarithms of the Initial Velocities of the Decomposition of H_2O_2 Experimentally Found (Log $v_{0,\mathrm{exptl}}$) at Different 2,2′-Bipyridyl Excesses, Corresponding with Figure 3, with Values Calculated in Several Ways (Log $v_{0,\mathrm{calcd}}$)

I			II		III			IV		
pH	[bipy]$_{\mathrm{tot}}$[a]	Log $v_{0,\mathrm{exptl}}$	[Cu(bipy)][b]	Log $v_{0,\mathrm{calcd}}$	[Cu(bipy)][c]	[Cu(bipy)(OH)][c]	Log $v_{0,\mathrm{calcd}}$[d]	[Cu(bipy)][e]	[(Cu(bipy)-(OH)$_2$][e]	Log $v_{0,\mathrm{calcd}}$[f]
6.0	4.00×10^{-4}	−3.02	3.64×10^{-4}	...	2.96×10^{-4}	7.43×10^{-5}	−3.01	3.61×10^{-4}	1.14×10^{-6}	−3.02
7.0	6.00×10^{-4}	−2.32	2.04×10^{-4}	−2.27	6.09×10^{-5}	1.53×10^{-4}	−2.25	1.60×10^{-4}	2.24×10^{-5}	−2.37
7.0	8.00×10^{-4}	−2.65	4.42×10^{-5}	−2.93	2.14×10^{-5}	5.38×10^{-5}	−2.70	4.25×10^{-5}	1.57×10^{-6}	−2.95
8.0	1.00×10^{-3}	−2.45	8.10×10^{-6}	−2.67	3.47×10^{-6}	8.72×10^{-5}	−1.62	7.37×10^{-6}	4.73×10^{-6}	−2.71
8.0	1.28×10^{-3}	−2.55	2.30×10^{-6}	−3.22	1.67×10^{-6}	4.21×10^{-5}	−1.94	2.28×10^{-6}	4.53×10^{-7}	−3.22
9.0	2.00×10^{-3}	−2.57	4.14×10^{-7}	−2.96	2.80×10^{-7}	7.05×10^{-5}	−0.73	4.07×10^{-7}	1.44×10^{-6}	−2.97
9.5	4.00×10^{-3}	−2.53	5.45×10^{-8}	−3.34	4.71×10^{-8}	3.75×10^{-5}	−0.50	5.43×10^{-8}	2.57×10^{-7}	−3.34

[a] In all cases $[Cu^{2+}]_{\mathrm{tot}} = 4 \times 10^{-4}$ *M*; $[H_2O_2]_{\mathrm{tot}} = 8 \times 10^{-3}$ *M*; *cf.* Figure 3. [b] Calculated with a computer (IBM 1620) with the aid of the constants given by Irving and Mellor.[9,10] [c] Calculated (IBM 1620) with reported constants,[10] taking into account the hydrolysis after Martell, *et al.*:[11] $([Cu(bipy)OH][H^+])/[Cu(bipy)] = 10^{-6.60}$. [d] Calculated on the supposition that $[Cu(bipy)]^{2+}$ and $[Cu(bipy)OH)]^+$ are equivalent catalysts. [e] Calculated (IBM 1620) with reported constants,[10] taking into account the hydrolysis after Perrin and Sharma:[12] $([(Cu(bipy)OH)_2][H^+]^2)/[Cu(bipy)]^2 = 10^{-11.06}$. [f] Calculated on the supposition that only $[Cu(bipy)]^{2+}$ is an efficient catalyst.

2,2′-bipyridyl was in excess, on the supposition that only the Cu^{2+}–2,2′-bipyridyl 1:1 complex is catalytically active (Table I). These calculated values (column II) agree with the values found experimentally (column I) for small but not for large excesses of 2,2′-bipyridyl (with respect to Cu^{2+}); *i.e.*, the calculated log $v_{0,\mathrm{calcd}}$ values are too small. This means the actually existing concentration of the catalyst is greater than supposed. The reason for this probably is found in the fact that these measurements were carried out at relatively high pH values where hydrolysis of the Cu^{2+}–2,2′-bipyridyl system occurs.[11,12]

If the complex ion, $[Cu(bipy)(OH)]^+$, is included in the calculations with the aid of the data of Martell, *et al.*,[11] one can see that it appears in considerable concentrations. From a new calculation of log $v_{0,\mathrm{calcd}}$ on the supposition that $[Cu(bipy)]^{2+}$ and $[Cu(bipy)(OH)]^+$ are equivalent catalysts, one obtains calculated values (column III) which are too high compared with the experimental ones. Probably the reason for this is that $[Cu(bipy)(OH)]^+$ is a poorer catalyst than $[Cu(bipy)]^{2+}$, since $[Cu(bipy)(OH)]^+$ has fewer "free" coordination positions. From the Cu^{2+}–glycinamide and Cu^{2+}–glycinamide–OH systems, such differences are known.[3]

Another possibility that may explain these results is the following. According to Perrin and Sharma,[12] only the binuclear complex $[Cu(bipy)(OH)]_2{}^{2+}$ exists in large concentrations during the hydrolysis of the Cu^{2+}–2,2′-bipyridyl system. This complex should be catalytically inactive, since the metal ion in it is coordinatively saturated.[3,13] If one calculates the concentration of $[Cu(bipy)]^{2+}$, taking into account $[Cu(bipy)(OH)]_2{}^{2+}$, and then after eq 2 log $v_{0,\mathrm{calcd}}$ (column IV), one again finds the values are too small.

The reason that the experimental values found in the presence of large excesses of 2,2′-bipyridyl do not agree with the calculated ones, even if one takes hydrolysis into account, probably comes from the fact that these measurements had to be carried out at relatively high pH values where the concentration of HOO^- increases. Thus, there may be considerable concentrations of ternary Cu^{2+}–peroxo–bipyridyl complexes, and indeed the reaction solutions are slightly yellow, which suggests that Cu^{2+}–peroxo complexes are formed.[3,4] These complexes could not be taken into account, since their stability constants are not known (*cf.* ref 6). Aside from this, it cannot be assumed that $[Cu(bipy)_2]^{2+}$, which occurs in higher concentrations under the conditions given for Figure 3, is an effective catalyst, since fourfold coordinated Cu^{2+} complexes like the Cu^{2+}–cyclam and the Cu^{2+}–phthalocyaninetetrasulfonic acid complexes are catalytically inactive.[14]

In the following discussion, we will restrict ourselves to the investigations done with Cu^{2+}:bipyridyl = 1:1 and in the pH range approximately 5.5–7.5 (Figures 1 and 2) where it is obvious that the Cu^{2+}–2,2′-bipyridyl 1:1 complex is the catalyst.

Discussion

The kinetic results summarized in eq 2 can be explained with eq 3–6, if one assumes that equilibria 3–5

$$H_2O_2 \overset{K_1}{\rightleftharpoons} HOO^- + H^+ \tag{3}$$

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

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

$$[Cu(bipy)(OOH)(H_2O_2)]^+ \xrightarrow{k^*} [Cu(bipy)]^{2+} + O_2 + H_2O + OH^- \tag{6}$$

favor reactants on the left side;[15] *i.e.*, the concentrations of the complexes $[Cu(bipy)(OOH)]^+$ and $[Cu(bipy)(OOH)(H_2O_2)]^+$ are small.

A postulation of the rate-determining step in equilibrium 5 would also be in accord with the experimental results. But our feeling is that the second H_2O_2 molecule also coordinates, and the rate-determining step consists of eq 6. This feeling originates from the observation that the catalytic activity of Cu^{2+}–glycinamide is affected by the coordination of a hydroxyl ion, while

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(11) A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback, and H. Hyytiainen, *J. Amer. Chem. Soc.*, **79**, 3036 (1957).

(12) D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 1271 (1966).

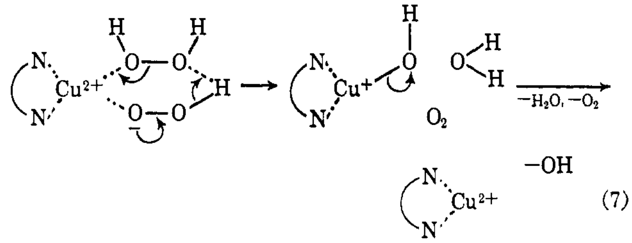
(13) In aqueous solution Cu^{2+} is tetracoordinate and shows little tendency to add more than four monodentate ligands or two bidentate ligands; *cf.* D. D. Perrin, I. G. Sayce, and V. S. Sharma, *J. Chem. Soc.*, *A*, 1755 (1967).

(14) H. Erlenmeyer, P. Waldmeier, and H. Sigel, *Helv. Chim. Acta*, **51**, 1795 (1968).

(15) In eq 3, this is certain, since $pK^{H}_{H_2O_2} = 11.8$: V. A. Kargin, *Z. Anorg. Allgem. Chem.*, **183**, 77 (1929).

the absorption at 360 nm (which indicates the formation of Cu^{2+}–peroxo complexes) is not.[16] A possible explanation for this is that for the formation of a simple Cu^{2+}–peroxo complex one "free" coordination position at the metal ion is necessary, but that the "active" complex needs two positions.[13] On the same line is a possible explanation for the decreasing catalytic activity in the series Cu^{2+}–iminodiacetic acid > Cu^{2+}–diethylenetriamine > Cu^{2+}–2,2′,6′,2′′-terpyridyl.[17] Within this series it probably becomes more and more difficult to get a second "free" coordination position for the formation of the "active" complex. Also Cu^{2+}–2,2′-bipyridyl is a much better catalyst than Cu^{2+}–2,2′,6′,2′′-terpyridyl.[17]

From the suggested mechanism in (3) through (6), the experimentally found eq 2 can be derived in which k becomes $k^*K_1K_2K_3$. For the structure of the assumed active complex, $[Cu(bipy)(OOH)(H_2O_2)]^+$, and its participation in decomposition of H_2O_2, the following scheme (eq 7) can be outlined. This scheme is similar to one tentatively proposed by us earlier.[17] It also has some similarities with the scheme of Erdey and Inczédy,[18] which was outlined for the alkaline decomposition of hydrogen peroxide. In this case the "cyclic" complex $[H_2O_2 \cdot OOH]^-$ is decomposed at the walls of the reaction vessel.



(7)

It is of interest that, based on the experimental results, a Cu^{2+} complex containing two molecules of H_2O_2, *i.e.*, H_2O_2 and HOO^-, can be postulated as the active species. Thus, it becomes possible that the whole reaction takes place within the coordination sphere of the metal ion. Hence, in accordance with earlier assumptions and results,[3] a mechanism for the reaction can be postulated without the formation of *free* radicals, as they occur, for example, in the mechanism postulated by Haber and Weiss[19] for the decomposition of hydrogen peroxide in the presence of iron ions (*cf.* also ref 20). Besides this, in contrast to the Cu^{2+}–ethylenediamine system (*cf.* ref 5), the reaction takes place through a monomeric complex. This shows that different mechanisms are possible for the catalysis of the decomposition of H_2O_2.

The larger catalytic activity of the Cu^{2+}–2,2′-bipyridyl 1:1 complex compared with the hydrated Cu^{2+} ion (*cf.* ref 8) may result from the fact that Cu^{2+} alone polymerizes and forms a precipitate under the conditions employed. Also it might be true that Cu^{2+}–2,2′-bipyridyl–peroxo complexes are more easily formed than Cu^{2+}–peroxo complexes, since ternary Cu^{2+}–2,2′-bipyridyl-O-ligand complexes are more stable than the corresponding binary Cu^{2+}–O-ligand complexes.[21]

Acknowledgments. We are grateful to Professor D. B. McCormick (Cornell University, Ithaca, N. Y.) for helpful comments. For making available the IBM computer 1620, we wish to thank the Rechenzentrum der Universität Basel. This work was supported by a grant from the CIBA-Stiftung (Basel).

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(16) H. Erlenmeyer, U. Müller, and H. Sigel, *Helv. Chim. Acta*, **49**, 681 (1966).

(17) H. Sigel and U. Müller, *ibid.*, **49**, 671 (1966).

(18) L. Erdey and I. Inczédy, *Acta Chim. Hung.*, **7**, 93 (1955).

(19) F. Haber and J. Weiss, *Proc. Roy. Soc.* (London), **A147**, 332 (1934); *Naturwissenschaften*, **20**, 948 (1932).

(20) N. Uri, *Chem. Rev.*, **50**, 375 (1952); J. H. Baxendale, *Advan. Catal.*, **4**, 31 (1952).

(21) H. Sigel, K. Becker, and D. B. McCormick, *Biochim. Biophys. Acta*, **148**, 655 (1967).