Contribution from the Institute of Inorganic Chemistry, University of Basel,
CH-4056 Basel, Switzerland

Metal Ions and Hydrogen Peroxide.[1] Catalase-like Activity of Cu^{2+} in Aqueous Solution and Its Promotion by the Coordination of 2,2′-Bipyridyl

HELMUT SIGEL,* KURT WYSS, BEDA E. FISCHER, and BERNHARD PRIJS

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The disproportionation of H_2O_2, catalyzed by Cu^{2+}(aq) and $Cu(2,2'\text{-bpy})^{2+}$, was investigated in the pH range of about 4–6.5 by measuring the initial rate, $v_0 = d[O_2]/dt$ ($M\ s^{-1}$), of the increase in the concentration of O_2 ($I = 0.1$, $NaClO_4$; 25 °C). The results can be summarized in the rate law $v_0 = k_M[M^{2+}][H_2O_2]^2/[H^+]$, where $M^{2+} = Cu^{2+}$ or $Cu(2,2'\text{-bpy})^{2+}$. This means the coordination of 2,2′-bipyridyl to Cu^{2+} does not alter the pathway of the reaction, which is outlined and discussed, but it does promote the catalytic activity by a factor of about 50: $k_{Cu} = 1.15 \times 10^{-6}\ M^{-1}\ s^{-1}$ and $k_{Cu(bpy)} = 5.44 \times 10^{-5}\ M^{-1}\ s^{-1}$. One of the reasons for this promotion is probably the enhanced stability of ternary complexes composed of a heteroaromatic N base (like 2,2′-bipyridyl), Cu^{2+}, and an O donor; further reasons could be an enhanced substitution rate and/or a facilitated electron transfer in the intermediate 2,2′-bipyridyl–Cu^{2+}–peroxo species. The influence of buffers on the catalase-like reaction is briefly mentioned, and possible reasons for the lower activity of Ni^{2+}(aq), which obeys the same rate law as is known from an earlier study ($k_{Ni} = 1.77 \times 10^{-9}\ M^{-1}\ s^{-1}$), are indicated.

The metal ion catalyzed disproportionation of H_2O_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.[2] Reaction 1 is also

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (1)$$

catalyzed by Cu^{2+} complexes,[3,4] provided the coordination sphere is accessible for H_2O_2 and/or HOO^- (cf. ref 3). Among the active complexes are the 2,2′-bipyridyl-containing species,[5] $Cu(bpy)^{2+}$ (cf. ref 6), and *cis*-$(H_2O)_2Cu(bpy)_2^{2+}$ (cf. ref 7 and 8). $Cu(bpy)^{2+}$ exhibits also a peroxidase-like activity,[9,10] as does *cis*-$(H_2O)_2Cu(bpy)_2^{2+}$ (cf. ref 11), and the reaction proceeds in all these cases within the coordination sphere of the metal ion.[3,6-9,11]

This observation means that the reaction proceeds via mixed-ligand complexes, and as we are interested in the relations between stability, structure, and reactivity of ternary complexes,[12-14] we studied the influence of 2,2′-bipyridyl on the catalase-like activity of Cu^{2+}. This was formerly not possible with the experimental methods accessible to us,[6] and in a study[15] on the catalytic activity of hydrated copper(II) the experimental conditions were too different from those[6,7] used for the Cu^{2+}/bpy systems to allow any comparisons. Now, the initial rate of the evolution of O_2, i.e., $v_0 = d[O_2]/dt$ ($M\ s^{-1}$), was measured with an oxygen-sensitive electrode. Both catalytic systems, Cu^{2+} and $Cu(bpy)^{2+}$, have the same rate law which is evidence that the reaction proceeds in both systems by the same mechanism, but the coordination of one 2,2′-bipyridyl to Cu^{2+} promotes its activity drastically, i.e., by a factor of about 50.

Experimental Section

Materials. $NaClO_4$, $Cu(ClO_4)_2\cdot 6H_2O$, and 2,2′-bipyridyl were from Fluka AG, Buchs, Switzerland. All the other reagents were the same as used earlier.[16,17]

Measurements and Evaluation. The concentration of O_2 in the reaction solutions was determined using a Beckman Fieldlab TM Oxygen Analyzer equipped with a rhodium/silver electrode (No. 39550) and a Walz+Walz recorder (Model 2011). The other apparatus and the further details were the same as those given earlier.[16,17]

The experiments were done exactly as described.[16,17] After pipetting of all reagents except H_2O_2 into the reaction vessel this solution was flushed with pure N_2 until the concentration of O_2 was about 2×10^{-6} M, or less. Then the reaction vessel was closed and the desired amount of oxygen-free H_2O_2 was injected through the capillary of the stopper. The increasing concentration of O_2 was recorded as a function of time.

In general no buffer was used in the experiments and the pH was adjusted with concentrated NaOH or $HClO_4$. As the pH was not stable, parallel experiments were carried out under exactly the same conditions: in one the O_2 concentration was measured and in the other the pH. In this way to each initial rate, v_0, the initial pH, i.e., pH_0, could be determined. For further details see Figure 1 in ref 17. The exact concentrations of all the reagents are given in the text and in the legends to the figures.

The data were evaluated[16] by plotting the logarithms of the initial rates, v_0, of the O_2 formation according to reaction 1 vs. the logarithms of the varied concentrations of the reagent. From the slope of the straight-line portion of the plots, the relationship between the reaction rate and the concentration of the corresponding reagent was taken.

Results

Cu^{2+}(aq) as Catalyst. First the dependence on pH of the initial rate of the catalyzed disproportionation of H_2O_2, i.e., $v_0 = d[O_2]/dt$ ($M\ s^{-1}$), was measured at a constant concentration of Cu^{2+} (10^{-3} M/$I = 0.1$, $NaClO_4$; 25 °C). Experiments at six different initial concentrations of H_2O_2 ($[H_2O_2]_{tot(t=0)} = 0.01–0.2$ M) were carried out. The results given in Figure 1a show that the initial rate of the reaction is proportional to $[H^+]^{-1}$. Evaluation of these results at constant pH (4.80) gives a straight line with a slope of 2 if $\log v_0$ is plotted vs. $\log [H_2O_2]_{tot(t=0)}$ (Figure 1b), i.e., v_0 is proportional to $[H_2O_2]^2$.

Corresponding experiments were also done in a wider pH range, i.e., 2 through 5.5, at $[Cu^{2+}]_{tot} = 10^{-4}$ M and $[H_2O_2]_{tot(t=0)} = 0.05–0.4$ M ($I = 0.1$, $NaClO_4$; 25 °C). In the pH range 2 to about 4 the rate of the reaction is independent of $[H^+]$, while at pH $\gtrsim 5$ v_0 is again proportional to $[H^+]^{-1}$. For both the pH dependent and the pH independent reactions v_0 is proportional to $[H_2O_2]^2$. Attempts to determine the relation between the initial rate of the catalysis and the concentration of Cu^{2+} for the pH-independent part of the reaction were not satisfactory[18] and therefore this part was not studied further, though it should be noted that Cu^{2+}-free reaction solutions showed no catalysis.

In another series of experiments the relation between the initial rate of the reaction and the concentration of Cu^{2+} for the pH dependent part of the catalysis (cf. Figure 1a) was determined at constant $[H_2O_2]_{tot(t=0)}$ (0.05 M) and varied $[Cu^{2+}]_{tot}$ (10^{-4}–5×10^{-3} M). From the results assembled in Figure 2 it is obvious that v_0 is proportional to $[Cu^{2+}]$. Hence, for the pH range of about 4–5.5 and the given concentrations of the reactants the results can be summarized by the rate law (2), where $k = (1.15 \pm 0.14) \times 10^{-6}\ M^{-1}\ s^{-1}$. The activation

$$v_0 = \frac{d[O_2]}{dt} = k\frac{[Cu^{2+}][H_2O_2]^2}{[H^+]} \qquad (2)$$

energy ΔE for this Cu^{2+}-catalyzed disproportionation of H_2O_2

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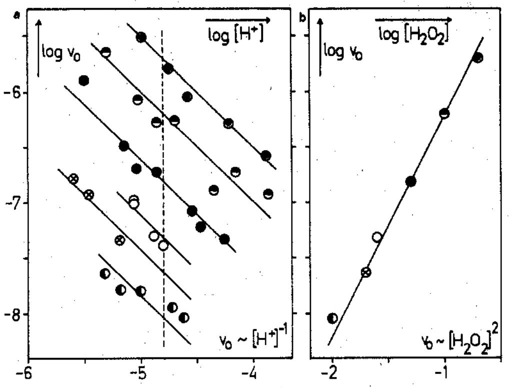

Figure 1. (a) Catalase-like activity of $Cu^{2+}(aq)$ (10^{-3} M) at different initial concentrations of H_2O_2 ($[H_2O_2]_{tot(t=0)}$: ◐, 0.01 M; ⊗, 0.02 M; ○, 0.025 M; ●, 0.05 M; ◓, 0.10 M; ◉, 0.20 M) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution (I = 0.1, $NaClO_4$; 25 °C). (b) Evaluation of the data of Figure 1a by plotting log v_0 vs. log $[H_2O]_{tot(t=0)}$ at constant pH, i.e., pH_0 4.80.

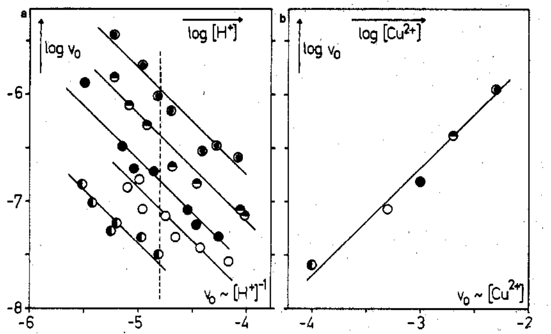

Figure 2. (a) Catalase-like activity of $Cu^{2+}(aq)$ at a constant initial concentration of H_2O_2 (0.05 M) but different concentrations of Cu^{2+} (◐, 10^{-4} M; ○, 5×10^{-4} M; ●, 10^{-3} M; ◓, 2×10^{-3} M; ◉, 5×10^{-3} M) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution (I = 0.1, $NaClO_4$; 25 °C). (b) Evaluation of the data of Figure 2a by plotting log v_0 vs. log $[Cu^{2+}]$ at constant pH, i.e., pH_0 4.80.

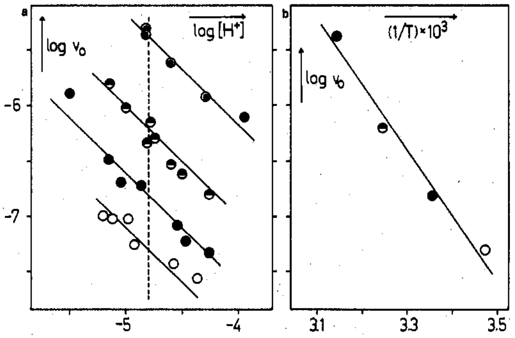

Figure 3. (a) Catalase-like activity of $Cu^{2+}(aq)$ (10^{-3} M) at a constant initial concentration of H_2O_2 (0.05 M) but different temperatures (○, 15 °C; ●, 25 °C; ◓, 35 °C; ◉, 45 °C) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution (I = 0.1, $NaClO_4$). (b) Evalution of the results of Figure 3a by plotting log v_0 vs. $1/T$ (in K) at constant pH, i.e., pH_0 4.80. Slope of the best (least squares) straight line: $m = -5.87 \times 10^3$. Activation energy, $\Delta E = -m(R/0.434) = 113$ kJ/mol.

was determined from experiments between 15 and 45 °C (Figure 3): $\Delta E = 113$ kJ/mol.

The Cu^{2+}/2,2′-Bipyridyl System. It has been observed earlier[6] that increasing concentrations of 2,2′-bipyridyl inhibit the catalase-like activity of a Cu^{2+}/bpy 1:1 system; i.e., the *cis*-$(H_2O)_2Cu(bpy)_2^{2+}$ species[7] is a less effective catalyst. In a Cu^{2+}/bpy 1:1 system about 90% of $[Cu^{2+}]_{tot}$ is present[6,7] as $Cu(bpy)^{2+}$ and only about 4.5%[7] as the less effective $Cu(bpy)_2^{2+}$; hence in a 1:1 system the catalase-like activity is practically completely determined by the activity of $Cu(bpy)^{2+}$. It is the present aim to evaluate further the catalase-like properties of this latter species.

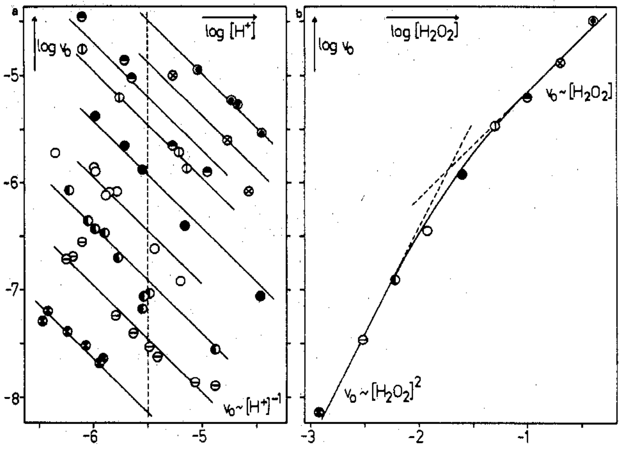

Figure 4. (a) Catalase-like activity of the Cu^{2+}/bpy 1:1 system ($[Cu^{2+}]_{tot} = [bpy]_{tot} = 5 \times 10^{-4}$ M) at different initial concentrations of H_2O_2 ($[H_2O_2]_{tot(t=0)}$: ◍, 0.0012 M; ⊖, 0.003 M, ◐, 0.006 M; ○, 0.012 M; ●, 0.025 M; ⦶, 0.05 M; ◓, 0.10 M, ⊗, 0.20 M; ◉, 0.40 M) in dependence on pH determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution (I = 0.1, $NaClO_4$; 25 °C). (b) Evaluation of the data of Figure 4a by plotting log v_0 vs. log $[H_2O_2]_{tot(t=0)}$ at constant pH, i.e., pH_0 5.5.

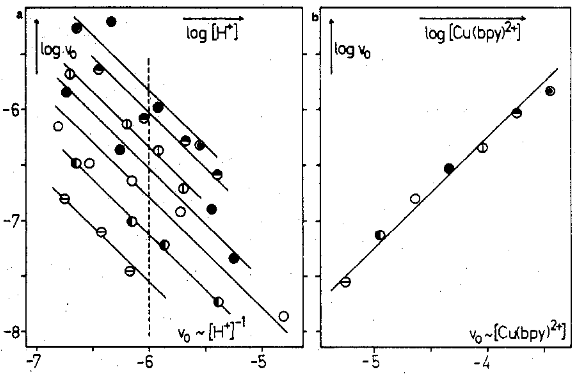

Figure 5. (a) Catalase-like activity of the Cu^{2+}/bpy 1:1 system at a constant initial concentration of H_2O_2 (0.01 M) but different concentrations of Cu^{2+} and 2,2′-bipyridyl ($[Cu^{2+}]_{tot} = [bpy]_{tot}$: ⊖, 6.25×10^{-6} M; ◐, 1.25×10^{-5} M; ○, 2.5×10^{-5} M; ●, 5×10^{-5} M; ⦶, 10^{-4} M; ◓, 2×10^{-4} M; ◉, 4×10^{-4} M) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution (I = 0.1, $NaClO_4$; 25 °C). (b) Evaluation of the data of Figure 5a by plotting log v_0 vs. log $[Cu(bpy)^{2+}]$ (calculated[20] from the total concentrations given for Figure 5a) at constant pH, i.e., pH_0 6.0.

The initial rate of the catalyzed ($[Cu^{2+}/bpy]_{tot} = 5 \times 10^{-4}$ M) disproportionation is again proportional to $[H^+]^{-1}$ (Figure 4a) in a whole series of experiments ($[H_2O_2]_{tot(t=0)}$ = 0.0012–0.4 M (I = 0.1, $NaClO_4$; 25 °C)). Evaluation of these data at a constant pH (5.5) results in a curve with a slope of 2 for lower concentrations of H_2O_2 and a slope of 1 for higher concentrations of H_2O_2 (Figure 4b). Saturation of the catalyst could not be reached in this series of experiments nor in a corresponding series where $[Cu^{2+}/bpy]_{tot} = 10^{-4}$ M and $[H_2O_2]_{tot(t=0)}$ = 0.001–0.4 M (I = 0.1, $NaClO_4$; 25 °C). Again the slope changed only from 2 to 1 thus preventing a detailed evaluation of the stability[19] and rate constants as it had previously been possible with cobalt(III)–hematoporphyrin as catalyst.[20,22] Therefore we restricted the present study to those conditions where v_0 is proportional to $[H_2O_2]^2$.

In another series of experiments (Figure 5a) the dependence of v_0 on the concentration of Cu^{2+}/bpy (6.25×10^{-6} to 4×10^{-4} M) was measured at constant $[H_2O_2]_{tot(t=0)}$ (10^{-2} M). The plot of log v_0 vs. log $[Cu(bpy)^{2+}]$ shows that v_0 is proportional

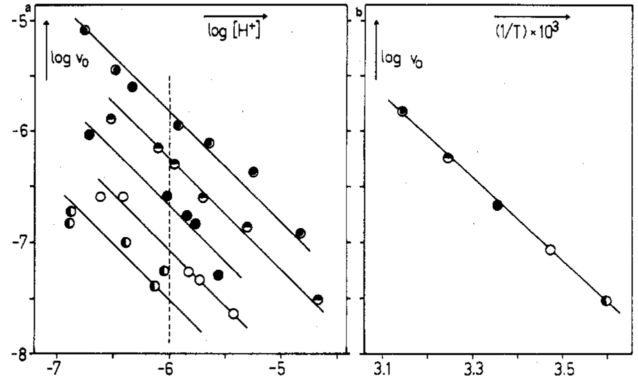

Figure 6. (a) Catalase-like activity of the Cu^{2+}/bpy 1:1 system (10^{-4} M) at a constant initial concentration of H_2O_2 (5×10^{-3} M) but different temperatures (◐, 5 °C; ○, 15 °C; ●, 25 °C; ⊖, 35 °C; ◉, 45 °C) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O_2 evolution ($I = 0.1$, $NaClO_4$). (b) Evaluation of the results of Figure 6a by plotting log v_0 vs. $1/T$ (in K) at constant pH, i.e., pH_0 6.0. Slope of the best (least squares) straight line: $m = -3.71 \times 10^3$. Activation energy, $\Delta E = -m(R/0.434) = 71$ kJ/mol.

to $[Cu(bpy)^{2+}]$ (Figure 5b).[23] Hence, for the pH range of about 4.5–6.5 and the given concentrations of the reactants (about: $[H_2O_2]_{tot(t=0)} \leq 1.2 \times 10^{-2}$ M; $[Cu^{2+}/bpy]_{tot} \leq 5 \times 10^{-4}$ M) the results can be summarized by the rate law (3),

$$v_0 = \frac{d[O_2]}{dt} = k\frac{[Cu(bpy)^{2+}][H_2O_2]^2}{[H^+]} \quad (3)$$

where $k = (5.44 \pm 1.25) \times 10^{-5}\ M^{-1}\ s^{-1}$. The activation energy ΔE for this system was determined from experiments between 5 and 45 °C (Figure 6); $\Delta E = 71$ kJ/mol.

Rate law 3 is identical with the one obtained earlier,[6] where about the same concentration ranges of the reactants had been covered, but the experiments were done at natural ionic strength (25 °C). However, the rate constant k obtained now is by a factor of about 6 smaller compared with the values determined earlier: 3.4×10^{-4} (ref 6) and $3.1 \times 10^{-4}\ M^{-1}\ s^{-1}$ (ref 7).[24] This difference may be partly due (up to a factor of about 2, in the maximum) to the differences in ionic strength (see the following section), but it is mainly the results of the different experimental methods employed. Formerly[6,7] the decreasing concentration of H_2O_2 had been determined with titanyl sulfate in 1.5 M H_2SO_4, and the *first* sample could only be taken after about 15 s (connected with a relatively large individual error),[25] while now the increasing concentration of O_2 was measured and the evaluation of the whole experiment was done approximately *within* the first 15 s. These different experimental procedures do lead automatically to somewhat different values for v_0 and especially to different values for the initial pH, i.e., pH_0, and this is the main reason for the observation of different rate constants. Indeed, in an experiment where the pH was kept constant with a pH stat[26] (and with reactant concentrations usable by both methods) the initial rates of the reaction determined by both methods were identical within experimental error, i.e., $v_0 = d[O_2]/dt = -0.5d[H_2O_2]/dt$ (cf. eq 1). Hence, rate constants of different catalytic systems should only be compared and used for conclusions if the constants have been obtained by the same experimental method. However, it should also be stressed that the different methods do lead to the same rate law, as was shown now for the $Cu(bpy)^{2+}$ system.[25]

Influence of Buffers and Ionic Strength. In an earlier study[17] on the catalase-like activity of Ni^{2+} and some of its complexes it became evident that buffers usually inhibit the catalysis, due to the coordinating properties of the buffer components, but that in certain cases, e.g., with borate, also an enhanced reactivity may be observed.

Therefore, with Cu^{2+} as catalyst (10^{-3} M) also series of experiments (25 °C) were carried out ($[H_2O_2]_{tot(t=0)} = 0.05$ M) at natural ionic strength, in 0.1 M $NaClO_4$, and in 0.1 M $NaClO_4$ with 0.1 M H_3BO_3. From Figure 7 (right-hand side) it is evident that the change in ionic strength might have a small influence on the rate of the reaction, but the additional presence of boric acid has obviously no effect (see also ref 8). This is understandable as in this pH range practically no borate exists and boric acid is probably not able to coordinate to the catalyst. Experiments in the presence of phosphate could not be carried out because a precipitate is formed, and experiments with 0.1 M acetate buffer revealed that the catalysis is completely inhibited, which indicates that the coordination sphere of Cu^{2+} is not readily accessible anymore to H_2O_2 and/or HOO^- due to the coordination of acetate. In fact, the possibility of such coordination reactions is the reason the experiments shown in Figures 1–6 were done in buffer-free systems.

Corresponding results were obtained with $Cu(bpy)^{2+}$ as catalyst ($[Cu^{2+}/bpy]_{tot} = 10^{-4}$ M; $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-2}$ M; 25 °C): this means 0.1 M H_3BO_3 has no influence while 0.05 M phosphate ($[Na^+] = 0.1$ M) and 0.1 M acetate completely inhibit the catalysis. Additionally, it appears that the system ($[Cu^{2+}/bpy]_{tot} = 10^{-4}$ M; $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-3}$ M) is somewhat more active at natural ionic strength than in 0.1 M $NaClO_4$ (cf. Figure 7; left-hand side).

Discussion

Reaction Mechanism. The kinetic results summarized in eq 2 and 3 for Cu^{2+} and $Cu(bpy)^{2+}$, respectively, indicate that the catalysis proceeds with both catalysts via the same mechanism, because both rate laws are of the same form. Accordingly, the following pathway may be outlined for both catalysts, where $M^{2+} = Cu^{2+}$ or $Cu(bpy)^{2+}$:

$$M^{2+} + H_2O_2 \rightleftharpoons M(H_2O_2)^{2+} \quad (4)$$

$$M(H_2O_2)^{2+} \rightleftharpoons M(OOH)^+ + H^+ \quad (5)$$

$$M(OOH)^+ + H_2O_2 \rightleftharpoons M(OOH)(H_2O_2)^+ \quad (6)$$

$$M(OOH)(H_2O_2)^+ \rightarrow M^{2+} + O_2 + H_2O + OH^- \quad (7)$$

Under the experimental conditions for which rate laws 2 and 3 hold, equilibria 4–6 are on the left side and the rate-determining step of the catalysis occurs in eq 7.

A mechanism in which eq 4 and 5 are replaced by eq 8 and 9 would also be in accordance with the rate laws.[6] However,

$$H_2O_2 \rightleftharpoons HOO^- + H^+ \quad (8)$$

$$M^{2+} + OOH^- \rightleftharpoons M(OOH)^+ \quad (9)$$

for the cobalt(III) hematoporphyrin/H_2O_2 system[22] evidence was given[20] that H_2O_2 is first coordinated and in the next step deprotonated. The same may be surmised for the present systems and therefore mechanism (4)–(7) is favored. In any case, there is no need to formulate a "chain ion–radical mechanism" for the Cu^{2+}-catalyzed disproportionation of H_2O_2 as has been postulated earlier.[15] There is now much evidence[3,4,6,8] that the reactions involving Cu^{2+} complexes and H_2O_2 proceed within the coordination sphere of the metal ion, and the mechanism proposed above is also in agreement herewith.

Structures for the species $M(OOH)(H_2O_2)^+$, in which the rate-determining step occurs (eq 7), have already been suggested earlier.[3,6,17] There is now a general agreement that the electron transfer occurs within such a species and that the orbitals of the metal ion are participating in this transfer.[3,4,6–9,17,20,22] The involvement of a cupric–cuprous couple in the reaction path, with a short lifetime of the Cu^I inter-

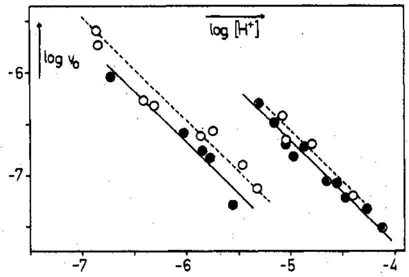

Figure 7. Comparison of the catalase-like activity of Cu^{2+} (10^{-3} M; right-hand side) and of the Cu^{2+}/bpy 1:1 system ($[Cu^{2+}]_{tot} = [bpy]_{tot} = 10^{-4}$ M; left-hand side) at natural ionic strength (○/dashed line), in 0.1 M NaClO$_4$ (●/full line), and in 0.1 M NaClO$_4$ with 0.1 M H$_3$BO$_3$ (◉) in dependence on pH, determined as the initial rate, v_0 (M s^{-1}), of the O$_2$ evolution (for Cu^{2+}, $[H_2O_2]_{tot(t=0)} = 0.05$ M; for Cu^{2+}/bpy, $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-3}$ M; 25 °C). For the influence of phosphate and acetate see text.

mediate, has been suggested,[3,4,8] and this seems indeed very attractive, although it should be mentioned that Cu^{2+}/peroxo systems tend to be slightly yellow due to an absorption in the 360-nm region[3,4,6,27] and that recently it has been reported[28] that a dimer copper(III) hydroxide species absorbs in the same part of the spectrum. Whatever the formal oxidation state of the transient intermediate may actually be, it should be noted in this connection that only those transition-metal ions (or their complexes) are catalytically active which have partly filled d orbitals.[3] Ions like Zn^{2+} or Cd^{2+} are catalytically inactive, which indicates that in the intermediate the electron transfer occurs through the metal ion.

Comparison of Catalysts. For the catalase-like activity of Ni^{2+} a rate law corresponding to eq 2 was observed[17] by the same method used now and therefore the rate constants for the catalysis by Ni^{2+} and Cu^{2+} may directly be compared: $k_{Ni} = 1.77 \times 10^{-9}$ M^{-1} s^{-1} (ref 17) and $k_{Cu} = 1.15 \times 10^{-6}$ M^{-1} s^{-1}. Obviously Cu^{2+} is a more effective catalyst by a factor of nearly 10^3. This could be explained by a "lower redox reactivity" of Ni^{2+}, i.e.,[29] it is more difficult for this metal ion to change its oxidation state than it is for Cu^{2+}, or by the smaller substitution rates[30] of Ni^{2+}(aq) compared with those of Cu^{2+}(aq). However, the fact itself that both aquated metal ions obey the same rate law in the catalyzed disproportionation of H$_2$O$_2$ is also most interesting because this does not hold for their complexes:[5] Ni^{2+} and Ni(en)$_2$$^{2+}$ have the same rate law (analogous to eq 2) but the complex is less active, while the rate law for the Ni^{2+}/bpy 1:1 system is different;[17] on the contrary Cu^{2+} and Cu(bpy)$^{2+}$ follow the same rate law as shown now, while the Cu^{2+}/en system[3] has a different one.

However, the most remarkable result of the present study is certainly that the coordination of 2,2′-bipyridyl to Cu^{2+} does not alter the reaction path but lowers the activation energy and does enhance the rate of the reaction considerably, i.e., by a factor of about 50 ($k_{Cu} = 1.15 \times 10^{-6}$ M^{-1} s^{-1}; $k_{Cu(bpy)} = 5.44 \times 10^{-5}$ M^{-1} s^{-1}). This corresponds with the observation that "chelation of Cu^{2+} by 1,10-phenanthroline and histidine greatly enhances its catalytic effect on the oxidation of glutathione" to its disulfide-containing oxidized form,[31] and it contrasts with results[32] which "suggest that change in ligand environment in "simple" complexes does not substantially alter the activity of the Fe^{III} center" in catalatic reactions.

The promoting effect of 2,2′-bipyridyl on the catalase-like activity of Cu^{2+} may in part be explained by the general observation[13] of an increased stability of the ternary complexes formed between Cu(bpy)$^{2+}$ and O donors, compared with the binary complexes formed by Cu^{2+}(aq), in other words by an increased tendency toward formation of Cu^{2+}–peroxo complexes in the presence of 2,2′-bipyridyl. However, based on the present experience[13] this will explain only a factor of up to 5; hence other points are most certainly also of importance: these could be an enhanced substitution rate[33,34] and/or a facilitated electron transfer[35] in the intermediate 2,2′-bipyridyl–Cu^{2+}–peroxo species; both factors would result in a larger turnover number.

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Registry No. H$_2$O$_2$, 7722-84-1; Cu(OH$_2$)$_6$$^{2+}$, 14946-74-8; Cu(2,2′-bpy)$^{2+}$, 16482-45-4.

References and Notes

(1) Part 32 of the series. Part 31: Sigel, H.; Prijs, B.; Rapp, P.; Dinglinger, F. *J. Inorg. Nucl. Chem.* **1977**, *39*, 179.
(2) Jones, P.; Wilson, I. *Met. Ions Biol. Syst.* **1978**, *7*, 185.
(3) Sigel, H. *Angew. Chem.* **1969**, *81*, 161. Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 167.
(4) Sharma, V. S.; Schubert, J.; Brooks, H. B.; Sicilio, F. *J. Am. Chem. Soc.* **1970**, *92*, 822.
(5) Abbreviations: bpy, 2,2′-bipyridyl; en, ethylenediamine; $[A]_{tot}$, total concentration of the reagent A; $[H_2O_2]_{tot(t=0)}$, total initial concentration (i.e., at the beginning of the reaction) of H$_2$O$_2$.
(6) Sigel, H.; Flierl, C.; Griesser, R. *J. Am. Chem. Soc.* **1969**, *91*, 1061.
(7) Griesser, R.; Prijs, B.; Sigel, H. *J. Am. Chem. Soc.* **1969**, *91*, 7758.
(8) Davies, G.; Higgins, R.; Loose, D. J. *Inorg. Chem.* **1976**, *15*, 700.
(9) Erlenmeyer, H.; Flierl, C.; Sigel, H. *J. Am. Chem. Soc.* **1969**, *91*, 1065.
(10) Wellman, C. R.; Ward, J. R.; Kuhn, L. P. *J. Am. Chem. Soc.* **1976**, *98*, 1683.
(11) Marov, I. N.; Belyaeva, V. K.; Smirnova, E. B.; Dolmanova, I. F. *Inorg. Chem.* **1978**, *17*, 1667.
(12) Sigel, H. *Met. Ions Biol. Syst.* **1973**, *2*, 63.
(13) Sigel, H. *Angew. Chem.* **1975**, *87*, 391. Sigel, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 394.
(14) Sigel, H.; Fischer, B. E.; Prijs, B. *J. Am. Chem. Soc.* **1977**, *99*, 4489.
(15) Berdnikov, V. M. *Zh. Fiz. Khim.* **1973**, *47*, 1879; *Chem. Abstr.* **1973**, *79*, 118724y.
(16) Waldmeier, P.; Sigel, H. *Inorg. Chim. Acta* **1971**, *5*, 659.
(17) Sigel, H.; Wyss, K.; Waldmeier, P.; Griesser, R. *J. Coord. Chem.* **1974**, *3*, 235.
(18) One might interpret the experimental results obtained for the Cu^{2+} dependence as v_0 being proportional to [Cu^{2+}]; then the rate law for the pH-independent part of the catalysis would be $v_0 = d[O_2]/dt = k^*[Cu^{2+}][H_2O_2]^2$, where $k^* \simeq 0.07$ M^{-2} s^{-1}.
(19) On the basis of both mentioned series of experiments one may make a rough guess about the stability of the first adduct (see Discussion, eq 4) formed with H$_2$O$_2$: $\log K^{Cu(bpy)}_{Cu(bpy)(H_2O_2)} \simeq 2.6$ (I = 0.1, NaClO$_4$; 25 °C). This stability constant may be compared with the one of the 1:1 complex between H$_2$O$_2$ and cobalt(III) hematoporphyrin (CoHP),[20] i.e., with $\log K^{CoHP}_{CoHP(H_2O_2)} = 2.7$. Taking into account that in both complex centers the metal ion has a formal charge of 2 (in CoHP one positive charge of Co^{III} is neutralized by the deprotonated ring) and that in both cases two aquated positions (counting only the equatorial positions for Cu(bpy)$^{2+}$)[21] remain for the coordination of H$_2$O$_2$, we find that the two stability constants correspond well with each other.
(20) Sigel, H.; Pasternack, R. F. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1093.
(21) Walker, F. A.; Sigel, H.; McCormick, D. B. *Inorg. Chem.* **1972**, *11*, 2756.
(22) Waldmeier, P.; Sigel, H. *Inorg. Chem.* **1972**, *11*, 2174.
(23) The actual concentration of Cu(bpy)$^{2+}$ under the experimental conditions was calculated with the equilibrium constants given by: Anderegg, G. *Helv. Chim. Acta* **1963**, *46*, 2397. Cf. also: Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5222.
(24) It should be noted in this connection that $v_0 = d[O_2]/dt = -0.5d[H_2O_2]/dt$; cf. eq 1. This correction has been applied to the given values.
(25) The Cu(bpy)$^{2+}$ catalysis has also been studied with the titanyl sulfate method by students in advanced inorganic courses; representative results[24] are as follows: student (1) $k = 7.2 \times 10^{-5}$ M^{-1} s^{-1}, (2) 8.2×10^{-5} M^{-1} s^{-1}, (3) 1.5×10^{-4} M^{-1} s^{-1}, (4) 2.1×10^{-4} M^{-1} s^{-1}, (5) 2.8×10^{-4} M^{-1} s^{-1}. The obtained rate constant depends strongly on the individual skill and the way pH$_0$ was estimated; however, it should be stressed that all students obtained the same relations between v_0 and the concentration of the reactants; i.e., they confirmed rate law 3.
(26) We are grateful to PD Dr. H.-G. Seiler for making this instrument accessible to us.
(27) This absorption in dependence on pH goes parallel with the catalytic activity of copper complexes.[3]
(28) Gray, E. T., Jr.; Taylor R. W.; Margerum, D. W. *Inorg. Chem.* **1977**, *16*, 3047.
(29) Zell, R.; Sigel, H. *Helv. Chim. Acta* **1966**, *49*, 870.
(30) Miller Frey, C.; Stuehr, J. *Met. Ions Biol. Syst.* **1974**, *1*, 51.

(31) Rabenstein, D. L.; Guevremont, R.; Evans, C. A. *Met. Ions Biol. Syst.*, in press.
(32) Cf. p 225 in ref 2.
(33) Kowalak, A.; Kustin, K.; Pasternack, R. F. *J. Phys. Chem.* **1969**, *73*, 281.
(34) Pasternack, R. F.; Sigel, H. *J. Am. Chem. Soc.* **1970**, *92*, 6146.
(35) Augustin, M. A.; Yandell, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 370.

Contribution from the Department of Chemistry,
State University of New York, College at Brockport, Brockport, New York 14420

Anation of the *cis*-Diaqua(ethylenediamine)(oxalato)chromium(III) Complex Ion by Oxalate Species

THOMAS W. KALLEN,* WILLIAM C. STEVENS, and DAVID G. HAMMOND

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At pH 5 and 35.0 °C the *cis*-$Cr(C_2O_4)(NH_2CH_2CH_2NH_2)(H_2O)_2^+$ complex ion undergoes anation by oxalate species in aqueous solution to produce $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_2)^-$ and small quantities of $Cr(C_2O_4)_2(NH_2CH_2CH_2NH_3)(H_2O)$. The products of the anation reaction are unstable in this pH region and in turn undergo a series of reactions which leads ultimately to $Cr(C_2O_4)_3^{3-}$. The kinetics of the initial anation reaction have been investigated at temperatures from 20.0 to 40.0 °C, at pH values from 2.00 to 5.00, at formal oxalate concentrations from 0.050 to 0.300 F and at ionic strengths of 0.80 and 1.00 M in potassium nitrate media. Observed pseudo-first-order rate constants exhibit a complex hydrogen ion dependence and a mass law retarded first-order dependence on the formal oxalate concentration. These rate constants have been interpreted in terms of a mechanism in which ion pair formation between $HC_2O_4^-$ (K_B), $C_2O_4^{2-}$ (K_C) and the parent complex precede a common ligand interchange step (k_1). In general, $k_{obsd} = k_1K_C[H^+]([H^+] + K_2')[C_2O_4^{2-}]/\{K_2'([H^+] + K_{a1}) + K_C[H^+]([H^+] + K_2')[C_2O_4^{2-}]\}$, where K_2' is the acid dissociation constant of an associated hydrogen oxalate ion and K_{a1} is the first acid dissociation constant of the aqua ligands of the complex ion. At 25.0 °C and an ionic strength of 0.80 M, $pK_{a1} = 5.92$, $K_2' = (7.25 \pm 0.15) \times 10^{-4}$ M, $K_B = 1.35$ M^{-1}, $K_C = 4.70 \pm 0.08$ M^{-1}, and $k_1 = (1.44 \pm 0.05) \times 10^{-3}$ s^{-1}. In the stated temperature interval and at an ionic strength of 0.80 M, the activation parameters of k_1 were found to be $\Delta H^\ddagger = 18.1 \pm 0.4$ kcal mol^{-1} and $\Delta S^\ddagger = -10.7 \pm 1.4$ cal mol^{-1} K^{-1}. A two-step oxalate anation mechanism has been described for this complex ion and other oxalato complexes of chromium(III). The mechanism is initiated by one-ended dissociation and isomerization of an oxalato-*O,O′* ligand to the oxalato-*O,O* bonding mode. Associative interchange of an ion-paired oxalate species for an aqua ligand is proposed to occur in the second step as a direct consequence of ligand isomerization. This mechanism successfully explains differences in the nature of the activation parameters for oxalate anation of oxalato complexes and other complexes of chromium(III). It also generalizes to provide a water exchange mechanism for oxalato complexes of chromium(III) which does not limit the anation rate.

Introduction

The mechanism of substitution of an oxalate ion[1] for aqua ligands bonded to chromium(III) has been a frequent subject of investigation during the past 3 decades. During this time a variety of investigators have determined the kinetics parameters for the reaction of $Cr(H_2O)_6^{3+}$ with oxalic acid[2] and the hydrogen oxalate ion,[3-5] the reaction of $Cr(NH_3)_5(H_2O)^{3+}$ with the hydrogen oxalate and oxalate ions,[6] the reaction of $Cr(en)(H_2O)_4^{3+}$ with the hydrogen oxalate ion,[7] the reaction of $Cr(ox)(H_2O)_4^+$ with the hydrogen oxalate ion,[3-5,8] and the reaction of *cis*-$Cr(ox)_2(H_2O)_2^-$ with oxalic acid,[9] the hydrogen oxalate ion,[4,5,10] and the oxalate ion.[10]

Two general mechanistic features have emerged as a result of these studies. First, substitution of a bidentate oxalato-*O,O′* ligand occurs in a single observable step. Monodentate substitution of an oxalato-*O* ligand seems to be rate determining for the overall process; and chelation of the oxalato-*O* ligand must occur in a relatively rapid, associative, aqua ligand displacement step. The results of studies of the rate of oxalate substitution on $Cr(NH_3)_5(H_2O)^{3+}$ [6] and the rate of chelation of the monodentate oxalato-*O* ligand of the transient $Cr(NH_3)_5(-OCOCO_2)^+$ and $Cr(NH_3)_5(-OCOCO_2H)^{2+}$ reaction intermediates[11] strongly support this particular choice of reaction sequence. Second, ion–ion or ion–molecule association precedes the rate-determining ligand interchange step. Ion-pairing equilibrium constants have been determined from the rate data for the reaction of the hydrogen oxalate and oxalate ions with $Cr(NH_3)_5(H_2O)^{3+}$ [6] and *cis*-$Cr(ox)_2(H_2O)_2^-$,[10] and association preequilibria are generally assumed to precede the rate-determining step of the other anation reactions as well.

When all similarities in the oxalate substitution reactions of this series are considered, one might reasonably conclude that kinetic parameters would be similar for all systems or would at least exhibit a reasonable trend based upon the charge of the particular chromium(III) complex undergoing substitution. These expectations are not completely realized. Oxalate substitution rates exceed the rate of water exchange of $Cr(H_2O)_6^{3+}$,[12,13] $Cr(NH_3)_5(H_2O)^{3+}$,[14] and *cis*-$Cr(ox)_2(H_2O)_2^-$ [15,16] in a manner indicative of an associative interchange (I_a) substitution mechanism. However, activation enthalpies and entropies for oxalate substitution decrease as the charge of the complex ion decreases. These trends indicate an increase in associative character of the substitution reaction as the Coulombic interaction between the complex ion and the associated oxalate species is decreasing in strength. Clearly the opposite trend would be more reasonable.

It is quite possible that the composition of the coordination sphere of the parent complex is the source of the contradictory relationship between charge and reaction character. In this series, complex ions which have a formal charge lower than +3 contain one or two oxalato-*O,O′* ligands, and an oxalato ligand may activate an alternate substitution mechanism which has associative character. Data exist to support this possibility. Kallen[9] has suggested the involvement of an oxalato-*O,O′* ligand in the oxalate anation reaction of *cis*-$Cr(ox)_2(H_2O)_2^-$ to explain the similarity which exists between trans–cis isomerization rates and anation rates of this complex ion. Schenk and Kelm[5] have also shown that the volumes of activation for oxalate anation of the oxalato complexes, $Cr(ox)(H_2O)_4^+$ and *cis*-$Cr(ox)_2(H_2O)_2^-$, differ drastically from the volume of activation of the oxalate anation reaction of $Cr(H_2O)_6^{3+}$. However, it is difficult to base a strong mechanistic hypothesis on these data alone.

We have examined the kinetics of the oxalate anation reaction of *cis*-$Cr(ox)(en)(H_2O)_2^+$ to gain additional data which

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