Al(III). Other investigations into the scope and mechanistic aspects of metal ion catalyzed hydrolysis of fluorine-containing species are in progress. Presently there is optimism regarding application to certain C–F linkages. This type of interaction has practical consequence in addition to the theoretical application of the hard and soft acid–base theory to metal-catalyzed substitutions in a number of organic reactions.

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Catalatic Activity of Metal Chelates and Mixed-Ligand Complexes in the Neutral pH Region. II. Copper–Histidine

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Abstract: The catalytic decomposition of hydrogen peroxide by Cu–histidine complexes has been investigated in the pH range 6–8 in phosphate buffer (0.013 *M*) by a differential manometric technique. The kinetic data on the initial rates of O_2 evolution are explained by a second-order rate equation, first order with respect to the 1:1 Cu–histidine chelate, and first order with respect to the HOO^- anion. Chemical and spectrophotometric studies indicated that the reaction mechanism involves a cupric–cuprous couple. The mechanism of the catalatic activity agrees with previous studies in which it was deduced that the peroxide anion acts as a bidentate ligand occupying two adjacent free sites in the complex. The greater bond angle in the Cu(I) complex facilitates rupture of the peroxidic oxygen bond. The presence of an anionic group, COO^-, on the coordinating molecule considerably reduces the catalytic activity of its copper chelate. The esr spectra of Cu(II)–histidine–H_2O_2 solutions were obtained but did not provide positive evidence regarding the participation by free radicals or radical intermediates in the reaction mechanism. However, as expected from the steady state approximation in the kinetic treatment of the system, the concentration of these radicals would be too small to be detected by esr.

The complex compounds of copper and iron provide relatively simple models for investigating the mechanisms of action of vitally important types of enzymes. They catalyze the decomposition of hydrogen peroxide, and, in general, promote the oxidation of hydrogen donors such as alcohols, phenols, and amines. However, in the neutral pH region, relatively few quantitative studies of catalatic reactions of copper complexes from which reaction mechanisms can be deduced have been reported. The reasons for the scarcity of data are due to the complexity of the equilibria at neutral pH, *e.g.*, hydrolytic reaction, mixed ligand complexes, etc.[1] It was concluded[2,3] from previous investigations in this laboratory that the reaction mechanism involved a cupric–cuprous couple and that the catalytically active complex species possessed two nitrogen atoms coordinated to the central metal ion, leaving two adjacent sites free on the metal ion. The chelating ligands presently studied had only nitrogen atoms available for coordination. Now, the catalytic reactions involving copper–histidine complexes, which possess a carboxylic group as well as donor nitrogen atoms, have been examined. In addition to the kinetics of O_2 evolution, the esr spectra of Cu–histidine–H_2O_2 solutions have been studied to ascertain if the reaction involves free radical species as was postulated by Barb, *et al.*,[4,5] for Fe(III)–H_2O_2 systems. The results reported here indicate that the catalytically active species is the 1:1 copper(II)–histidine complex and the hydrogen peroxide anion, HOO^-. The esr spectra did not provide evidence for the participation of free radical species in the reaction mechanism.

In addition to the catalytic reaction between Cu–histidine and hydrogen peroxide, it is well known that histidine undergoes metal-catalyzed decarboxylation. However, at room temperature in aqueous solutions, the decarboxylation reaction can be ignored.[6] Histidine is also known to form an H_2O_2–histidine adduct.[7] As the equilibrium constant for the formation of this adduct is not known, no correction could be made for its concentration. To minimize the effect of these side

(1) J. Schubert, V. S. Sharma, E. R. White, and L. S. Bergelson, *J. Amer. Chem. Soc.*, **90**, 4476 (1968).
(2) V. S. Sharma and J. Schubert, *ibid.*, **91**, 6291 (1969).
(3) V. S. Sharma and J. Schubert, submitted for publication.
(4) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 591 (1951).
(5) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *ibid.*, **47**, 462 (1951).
(6) A. C. Andrews and E. W. Grundemeir, *J. Inorg. Nucl. Chem.*, **28**, 455 (1966).
(7) J. Schubert, J. A. Watson, and J. M. Baecker, *Int. J. Radiat. Biol.*, **14**, 577 (1969).

Table I. Observed Rate, R, of Hydrogen Peroxide Decomposition at 25° as a Function of pH in Solutions Containing Copper, Histidine, Hydrogen Peroxide, and Sodium Dihydrogen Phosphate[a]

Reading no.	pH	$R \times 10^8$, l. mol^{-1} sec^{-1}	Cu^{2+}	HD^-	PO_4^{3-}	HOO^-
1	6.45	2.90	1.080×10^{-6}	1.691×10^{-9}	2.084×10^{-8}	2.156×10^{-6}
2	6.89	3.44	4.403×10^{-7}	2.505×10^{-9}	9.691×10^{-8}	5.938×10^{-6}
3	7.41	3.37	1.337×10^{-7}	3.991×10^{-9}	4.424×10^{-7}	1.966×10^{-5}
4	7.60	2.88	8.141×10^{-8}	4.795×10^{-9}	7.275×10^{-7}	3.045×10^{-5}
5	7.68	3.85	6.536×10^{-8}	5.193×10^{-9}	8.916×10^{-7}	3.661×10^{-5}
6	7.74	3.517	5.522×10^{-8}	5.519×10^{-9}	1.036×10^{-6}	4.203×10^{-5}
7	7.20	3.03	2.987×10^{-7}	2.931×10^{-9}	2.474×10^{-7}	7.960×10^{-6}
8	7.20	6.18	4.351×10^{-7}	3.334×10^{-9}	2.470×10^{-7}	1.238×10^{-5}
9	7.20	6.17	8.669×10^{-7}	3.344×10^{-9}	2.459×10^{-7}	1.238×10^{-5}
10	7.20	3.76	1.545×10^{-6}	2.652×10^{-9}	2.449×10^{-7}	4.946×10^{-6}
11	7.20	2.92	1.905×10^{-6}	2.462×10^{-9}	2.444×10^{-7}	2.648×10^{-6}
12	7.20	2.01	2.007×10^{-6}	2.377×10^{-9}	2.443×10^{-7}	2.473×10^{-6}

[Sodium Phosphate Buffer]$_T$ = 0.013 M (for all readings)

$[Cu^{2+}]_T$	$[HD]_T$	$[H_2O_2]_T$	Reading no.
1.33×10^{-4}	1.33×10^{-4}	0.305	1–6
1.33×10^{-4}	1.33×10^{-4}	0.200	7
2.67×10^{-4}	2.67×10^{-4}	0.311	8
5.33×10^{-4}	5.33×10^{-4}	0.311	9
5.33×10^{-4}	5.33×10^{-4}	0.12	10
5.33×10^{-4}	5.33×10^{-4}	0.060	11
5.33×10^{-4}	5.33×10^{-4}	0.062	12

[a] The pK's for stability constants for species marked with an asterisk were calculated from the equations proposed in ref 10 and 11: H_3HD^{2+}, 17.04; H_2HD^+, 15.0; HD^-, 9.20;[12] H_3PO_4, 20.61; $H_2PO_4^-$, 18.5; HPO_4^{2-}, 11.8;[13] H_2O_2, 11.6;[14] $Cu(HD)^+$, 10.35; $Cu(HD)_2$, 18.7;[12] $Cu(H_2PO_4)^+$, 19.25; $Cu(HPO_4)$, 15.0;[13] $Cu(OH)^+$, −6.5; $Cu_2(OH)_2^{2+}$, −10.95;[15] $Cu(HD)(H_2PO_4)$*, 28.6; $Cu(HD)(HPO_4)$*, 24.35; $Cu(HOO)^+$, 6.45;[1] $Cu(HD)(HOO)$*, 15.80; $Cu(HD)(OH)$, 2.96; $Cu_2(HD)_2(OH)_2$, 8.55.[16]

reactions and oxidative destruction of the ligand and the chelate,[8] the kinetics of hydrogen peroxide decomposition were investigated only from the initial rates of O_2 evolution.

Experimental Section

Kinetic Runs. The rates of decomposition of H_2O_2 were determined from manometric measurements of O_2 by the use of a differential syringe manometer, as described earlier.[2] The kinetic runs were made at a total phosphate concentration of 0.013 M, inasmuch as the catalytic activity is very sensitive to buffer concentration. A high H_2O_2:Cu(II) ratio was maintained, since the kinetics of H_2O_2 decomposition are dependent on the relative concentrations of H_2O_2 and the metal ion.[4,5] No visible precipitation or turbidity was observed in solutions at any stage of the work.

The final pH of solutions was checked with an Orion digital pH meter. The pH standards taken were 0.05 M potassium hydrogen phthalate, pH 4.00 ± 0.02 at 25°, and 0.05 M potassium phosphate monobasic–sodium hydroxide buffer, pH 7.00 ± 0.02 at 25°. No attempt was made to convert the hydrogen ion activity into concentration, since the possible errors resulting from using the estimated values of several stability constants are considerably greater than that resulting from the neglect of activity correction.

Chemicals. Histidine (HD) free base Sigma Grade I was dried at 120° for 10 hr. All other reagents were as described earlier.[2]

Esr Runs. A Varian 4502-15 spectrometer equipped with V-4500 100-kHz field modulation and Fieldial units were used for the esr measurements. The flow system consisted of two reservoirs, polyethylene tubing, metering valves, a Varian 4549 liquid flow mixing chamber, and a Varian 4548 quartz aqueous solution cell.[9] The reactant solutions were deaerated with nitrogen and stored under a nitrogen pressure of 14 psi before the two streams were mixed. Equal flow rates were maintained for the individual streams. Total flow rate for the mixed stream was controlled by a needle valve on the exit tube. The mixed stream traversed a hold-up volume of 0.16 ml before reaching the sensitive portion of the flat cell in the resonant cavity of the spectrometer. Times between mixing and observation were calculated from the ratio of hold-up volume (ml): flow rate (ml/sec), and were varied from 20 to 200 msec. A few runs were also made between 200 msec and 2 sec by using a delay chamber between the mixer and flat cell. The latter runs were also observed statically as a function of time so that slow changes in the system could be observed.

Spectrophotometry. The absorption spectra of various combinations of histidine, copper, and hydrogen peroxide were taken using a UNICAM SP-800A double beam recording ultraviolet and visible spectrophotometer.

Results and Discussion

Solution Equilibria. In aqueous solutions containing copper(II), histidine, and hydrogen peroxide in phosphate buffer, the following equilibria are considered: (a) ionization of histidine and the formation of 1:1 and 1:2 Cu–histidine complexes; (b) ionization of hydrogen peroxide and the formation of a $[Cu \cdot OOH]^+$ complex; (c) ionization of H_3PO_4 into $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}; (d) formation of the copper complexes of $H_2PO_4^-$ and HPO_4^{2-}; (e) hydrolysis of Cu^{II} ions to give $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, and $Cu_3(OH)_4^{2+}$; (f) the formation of mixed complexes of histidine, phosphoric acid, and hydrogen peroxide; and (g) formation of hydrolyzed species of copper–histidine complexes such as $LCu \cdot OH$ and $L_2Cu_2(OH)_2$. In all, the formation of 19 species existing in dynamic equilibrium with each other has been taken into account. The equilibrium concentrations of various species were calculated on an IBM 360/50 computer as described earlier.[2] A listing of these species, together with the logarithms of their overall stability constants obtained from the literature as

(8) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

(9) E. L. Lewis and F. Sicilio, *J. Phys. Chem.*, **73**, 2590 (1969).

cited,[10-16] is given in the footnote to Table I. It is assumed that beyond pH 6, the formation of copper complexes of protonated histidine is relatively unimportant. From the knowledge of the stability constants, pH, free ligand (HD, PO_4^{3-}, HOO^-), and free metal ion concentration (listed in Table I), the concentration of any species listed in the footnote to Table I can be calculated. The concentrations of Cu-Hd^+, Cu(HD)(OH), Cu^{2+}, and HOO^- as a function of pH are plotted in Figure 1. It should be noted that the values

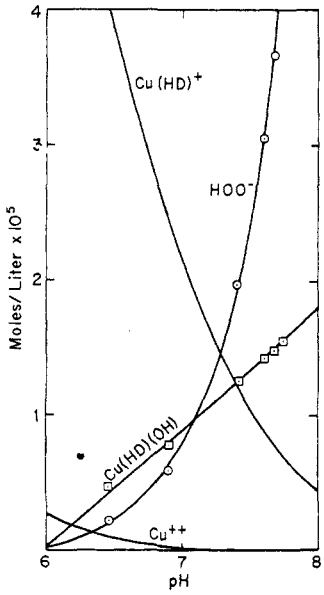

Figure 1. Concentration of $Cu(HD)^+$, Cu(HD)(OH), free Cu^{2+}, and peroxide anion as a function of pH. $[Cu^{2+}]_T = 1.33 \times 10^{-4}$, $[HD]_T = 1.33 \times 10^{-4}$, $[H_2O_2]_T = 0.305$, [sodium phosphate buffer]$_T$ = 0.013 *M*.

of several of these constants are somewhat uncertain and their cumulative effect on the calculated concentrations of the corresponding species will be a function of pH. Also, the possibility of species other than those postulated in the present investigation cannot be ruled out.

Kinetic Runs. The observed rates of O_2 evolution, *R*, were obtained from the initial slopes of a plot of microliters of O_2 evolved *vs.* time. However, due to the side reactions mentioned earlier, the initial slopes could be obtained only approximately. The microliters of O_2 evolved *vs.* time relationship was linear for rather a short time only. In all other details, the kinetic runs were made as described earlier.[2]

When the pH and histidine and copper concentrations were kept constant, and the total peroxide concentration was varied tenfold in the range 0.03–0.3 *M*, the rates of O_2 evolution were first order in total peroxide concentration. The dependence of the rate of O_2 evolution on the concentration of various copper complexes was studied by varying pH. The rate of O_2 evolution was first order in $Cu(HD)^+$ complex in the concentration range 6.2×10^{-5}–6.8×10^{-6} *M*, and first order in the HOO^- anion concentration (7.8×10^{-7}–4.2×10^{-5} *M*) (Figure 2). The rate expression, therefore, can be written as

$$R = k_1[CuL^+][HOO^-] \quad (1)$$

or

$$= k_1\beta_{11}[Cu^{2+}][L^-][HOO^-] \quad (2)$$

The rate constant, k_1, as obtained from the slope of the straight line in Figure 2 is 130 l. mol^{-1} sec^{-1}. This value is considerably less than the values of rate constants reported for Cu-(imidazole)$_2$-H_2O_2, Cu-ethylenediamine-H_2O_2, Cu-1,3,diaminopropane-H_2O_2, and Cu(II)-histamine-H_2O_2 systems, presumably due to the

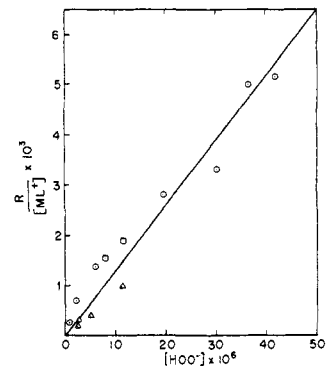

Figure 2. Graphical evaluation of rate constant, k_1, for hydrogen peroxide decomposition by Cu^{II}-HD chelate at 25°. The initial $[Cu^{2+}]_T$, $[HD]_T$, $[H_2O_2]_T$, and [phosphate buffer]$_T$ are the same as in Table I: reading 1–6, ⊙; 7, 8, ⊡; 9–12, △.

presence of an anionic group in the chelate. This is in agreement with the observations that the chelates of anionic ligands possess negative or less positive redox potentials[17] and are, therefore, less active toward hydrogen peroxide decomposition.[2,18]

Possible Mechanisms. The kinetic data fit eq 1 and 2 over a wide range of concentrations of HOO^- and ML^+ species. However, the data fit equally well to the equations

$$R = k_2[LCu^{II}OOH] \quad (3)$$

or

$$R = k_2\beta_{111}[Cu^{2+}][L^-][HOO^-] \quad (4)$$

In terms of free metal, free ligand, and peroxide anion concentrations, the two sets of equations are identical and differ only with respect to the formation constants, β_{11} and β_{111}, respectively. From the kinetic data alone, it is difficult to decide whether the reaction proceeds by

(10) V. S. Sharma and J. Schubert, *J. Chem. Educ.*, **46**, 506 (1969).
(11) Y. Kanemura and J. I. Watters, *J. Inorg. Nucl. Chem.*, **29**, 1701 (1967).
(12) D. D. Perrin, *Nature*, **184**, 1868 (1959).
(13) G. Schwarzenbach and G. Geir, *Helv. Chim. Acta*, **46** 906 (1963).
(14) M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).
(15) D. D. Perrin, *J. Chem. Soc.*, 3189 (1960).
(16) D. D. Perrin and V. S. Sharma, *ibid.*, *A*, 724 (1967).
(17) B. J. James and R. J. P. Williams, *ibid.*, 2007 (1961).
(18) J. H. Wang, *J. Amer. Chem. Soc.*, 77, 4715 (1955).

either one or both of these steps. Absorption spectra studies, however, indicate that a mixed-ligand complex, LCuOOH, is formed in these systems. Figure 3 shows absorption spectra of solutions containing various combinations of H_2O_2, histidine, and Cu^{2+}. Only in the presence of histidine is there a marked increase in the absorbance of solutions containing copper and hydrogen peroxide (pH $\approx$7.4). The absorption at $\approx$350 mμ (both in the presence and absence of histidine) most probably arises from charge transfer from peroxide anion to the cupric ion or its complex which is reduced to the cuprous state. The coordination of two nitrogens in the intermediate LCuOOH facilitates the electron transfer, giving increased absorption in this region. The parallelism between the absorption in this region and the catalytic activity of copper complexes has already been reported.[19]

One can explain the kinetic data and obtain eq 1, 2 and 3, 4 by assuming the following sequence of reactions.

$$2H_2O_2 \overset{k_a}{\rightleftharpoons} 2HOO^- + 2H^+ \qquad (5)$$

$$\underset{C}{LCu^{II}(H_2O)_2^+} + HOO^- \overset{-2H_2O}{\rightleftharpoons} \underset{C_1}{LCu^{II}HOO} \xrightarrow{k_2} \underset{C_2}{LCu^{I}HOO^-} \qquad (6)$$

$$LCu^{I}HOO^- + HOO^- \longrightarrow LCu^{II}(OH)_2^- + O_2 \qquad (7)$$

$$LCu^{II}(OH)_2^- + 2H^+ \rightleftharpoons LCu^{II}(H_2O)_2^+ \qquad (8)$$

In this reaction scheme, it is assumed that in the intermediate C_1, the peroxide anion acts as a bidentate ligand.[18] During the one-electron transfer from HOO^- to the Cu(II) complex, the latter is reduced to Cu(I). This causes the O–M–O bond angle to increase from 90° in square-planar Cu(II) complexes to 109° in the tetrahedral cuprous complexes. As a result of this change in the geometry of bonding orbitals of copper ion, the O–O bond in the bidentate peroxide anion will presumably rupture in the intermediate C_2.

The formation of the cuprous state was demonstrated by the development of a pink color[20] when 2,2′-biquinoline was added to copper–histidine–H_2O_2 solutions. The intermediate C_2 contains electron-deficient oxygen, and therefore, it can readily react with a second peroxide anion (eq 7). The mechanism proposed above is cyclic, but in actual practice an oxidative destruction[19,21] of the ligand and complex and the formation of an H_2O_2–histidine adduct does take place, and the reactions are probably not quantitatively cyclic. By confining the present studies to the initial rates, an attempt has been made to minimize the complications due to these side reactions.

Using the steady state approximation for the calculation of the concentration of the intermediate, [LCu^{I}-HOO], we get

$$R = d(O_2)/dt = k_2[LCu^{II}HOO] \qquad (9)$$

which is the same as eq 3. By assuming that, in eq 6 of the reaction scheme, C goes directly to C_2 (C $\rightarrow$ C_2 (k_1)) one obtains eq 1.

Esr Studies and Free Radical Mechanism. In studies on H_2O_2 decomposition by iron and its complex at low pH, Barb, *et al.*,[4,5] postulated free radical mechanisms as a result of the reduction of the ferric to ferrous state. In the present investigation, the polymerization of acrylonitrile in the presence of Cu(II)–H_2O_2 (pH $\approx$7) was employed to detect free radical formation, but no polymerization was observed despite precautions to exclude oxygen from the system. When the level of cuprous ions was increased by direct addition, however, polymer formation took place.

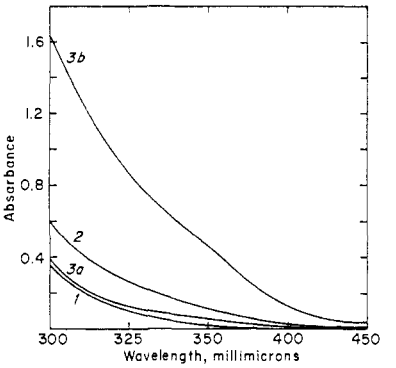

Figure 3. $[Cu^{2+}]_T$ = 0.0016, [histidine]$_T$ = 0.0032, $[H_2O_2]_T$ = 0.067, [phosphate buffer]$_T$ = 0.02 *M*, pH 7.4. 1, Cu^{2+} + histidine in phosphate buffer; 2, Cu–H_2O_2 (pH 7.2, solution not clear); 3, Cu^{2+} + histidine + H_2O_2 in phosphate buffer; (a) spectrum taken ~1 min after mixing H_2O_2 with solution 1; (b) $\approx$3 min after mixing. Both solutions, a and b, were clear.

In order to detect and identify the free radical species formed, if any, during the course of H_2O_2 decomposition by the copper–histidine complex, the esr spectrum of Cu(II)–histidine complex was observed in aqueous solutions both before and after mixing with hydrogen peroxide in near neutral pH regions. After 2 min, the signal from the Cu(II)–histidine complex changed from four esr signals, corresponding to $^3/_2$ spin of Cu(II) ion, to a single broad line characteristic of uncomplexed copper. This is presumably due to the oxidative breakdown of the complex by hydrogen peroxide. However, no change in peak area was observed, which suggested that if Cu(I) was formed its concentration was less than 5%—the minimum amount detectable. During the first minute, no change in the Cu(II)–chelate spectrum was observed. No new resonances due to radical intermediates were observed either. The copper–histidine concentration was varied from 0.0025 to 0.01 *M* and the hydrogen peroxide concentration was varied from 0.01 to 1.0 *M*. No free radical intermediates were observed at any concentration. However, this result does not exclude the presence of radicals in the system. The Fe(II)–H_2O_2 system has also been investigated by esr flow techniques[22] and no radicals were observed due to the reaction of Fe(II) with H_2O_2, even though chemical tests have shown that

(19) H. Sigel, *Angew. Chem.*, **8**, 167 (1969).
(20) I. M. Klotz and T. A. Klotz, *Science*, **121**, 477 (1955).
(21) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **51**, 935 (1955).
(22) F. Sicilio, R. E. Florin, and L. A. Wall, *J. Phys. Chem.*, 70, 47 (1966).

radicals are present.[4] One explanation for the negative results is that the OH radical is extremely reactive and the concentration at any time is too small to observe. This explanation would reaffirm the steady state approximation in the kinetic treatment of this system. Another explanation, presented by Dixon,[23] is that the hydrogen atoms in water exchange rapidly and the signal from OH is broadened.

$$HOH + OH \rightleftharpoons HOH^* + OH \qquad (10)$$

In the Fe(II)–H_2O_2 system, there was some indirect evidence for radical formation. When 1,4-butenediol was added to the Fe(II) solution, organic radicals were observed.[22] Thus, butenediol was used as a substrate in the copper–histidine system also. Initial concentrations of reactants were the same as concentrations used for radical production in the Fe(II)–H_2O_2 system (0.5 *M* butenediol, 0.1 *M* H_2O_2, 0.1 *M* Cu–histidine chelate). In separate runs, the diol was reduced to 0.2 *M*, and then the peroxide to 0.1 *M*. No substrate radicals were observed in any case.

The involvement of a cupric–cuprous couple in the reaction mechanism of hydrogen peroxide decomposition by copper chelates was indicated by the biquinoline test,[20] which is far more sensitive than the esr analysis.

(23) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).

Conclusions

The main conclusions of the present investigation are (1) the active species in the decomposition of hydrogen peroxide by copper–histidine chelates are the 1:1 copper–histidine complex and peroxide anion; (2) the splitting of the peroxide bond, O–O, is presumably brought about by the change in the stereochemistry of the complex due to reduction of the Cu(II) complexes to cuprous complexes; (3) the reaction is favored by an increase in pH; (4) the presence of an anionic group, COO^-, on the chelate reduces its catalytic activity toward hydrogen peroxide decomposition; (5) the esr studies do not provide evidence for the presence of free radicals or a radical intermediate in the H_2O_2–Cu–histidine system, and the kinetic data can be explained by a reaction mechanism that does not involve free radicals.

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The Cyclopentadienyls of Titanium, Zirconium, and Hafnium

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Abstract: The first synthesis of bis(cyclopentadienyl)hafnium is reported; numerous physical and chemical properties of this species are considered in relation to those of the titanium and zirconium analogs and the bis-cyclopentadienyls of other transitional metals.

In earlier publications the synthesis and certain chemical and physical properties of bis(cyclopentadienyl)titanium were described[1] and the first synthesis of the zirconium analog was announced.[2] Here the synthesis of the hitherto unreported bis(cyclopentadienyl)hafnium, its behavior upon oxidation, adduct formation with diphenylacetylene, and a comparison of its properties with those of certain other transitional metals are described.

In addition to prior work in this general area cited earlier,[1,2] the authors became aware belatedly of a reported synthesis of $(C_5H_5)_2Ti$ by Shikata *et al.*,[3] *via* the reduction of $(C_5H_5)_2TiCl_2$ with NaHg. They reported a carbon content 5% below the calculated value, and a very poorly resolved infrared spectrum. They did, however, find molecular weights indicative of $[(C_5H_5)_2Ti]_2$ in agreement with earlier results from this laboratory.[1] It seems likely that they did indeed produce $[(C_5H_5)_2Ti]_2$ but in rather low purity.

(1) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Amer. Chem. Soc.*, **88**, 1138 (1966).
(2) G. W. Watt and F. O. Drummond, Jr., *ibid.*, **88**, 5926 (1966).
(3) K. Shikata, K. Yokogawa, S. Nakao, and K. Azuma, *Kogyo Kagaku Zasshi*, **68** (7), 1248 (1965).

Experimental Section

Unless otherwise indicated, analytical methods and procedures for physical measurements were essentially the same as those reported previously.[1,2]

Synthesis of $(C_5H_5)_2Hf$. In an oxygen-free dry helium atmosphere, 3.6 g (9.46 mmol) of $(C_5H_5)_2HfCl_2$, 0.44 g (18.96 mg-atom) of Na, 3 g of $C_{10}H_8$ (*ca.* 15% molar excess), and a magnetic stirring bar were placed in a 250-ml flask. The pressure was reduced and