**Bond.**—Since the first phosphorus trifluoride complex was prepared,[5] it has generally been assumed that CO and PF$_3$ have much in common as ligands, since the bonding possibilities of the two are similar, and a number of studies have confirmed this viewpoint.[27–29]

The data obtained in this study of the substitution reactions of Ni(PF$_3$)$_4$ and Pt(PF$_3$)$_4$ provide new insight into the nature of the metal–PF$_3$ bond and its supposed similarity to metal–CO bonds. The activation parameters for substitution reactions of CO–, PF$_3$–, and P(OC$_2$H$_5$)$_3$–metal complexes of the nickel triad are collected in Table V. The first obvious conclusion to be drawn from these data is that in activation enthalpies, and hence presumably in bond strengths, the PF$_3$ complexes are more similar to the P(OC$_2$H$_5$)$_3$ complexes than to the CO complexes. It is suggested that the better $\pi$-acceptor ability of PF$_3$ makes up for its poorer $\sigma$-donor strength, when compared with P(OC$_2$H$_5$)$_3$, resulting in similar metal–phosphorus bond strengths.

Comparison of the enthalpies of activation for metal–ligand bond rupture in Ni(PF$_3$)$_4$ and Ni(CO)$_4$ indicates that the metal–PF$_3$ bond is considerably stronger than the metal–CO bond. Of course the enthalpies of activation are not equal to the bond dissociation energies unless the activation energies for the reverse reaction of eq 2 are zero. However in comparison of Ni(CO)$_4$ and Ni(PF$_3$)$_4$, it is considered unlikely that the activation energies of recombination of Ni(CO)$_3$ with CO and Ni(PF$_3$)$_3$ with PF$_3$ have very different values, and hence

(27) R. J. Clark and E. O. Brimm, *Inorg. Chem.*, **4**, 651 (1965).
(28) W. J. Miles, B. B. Garrett, and R. J. Clark, *ibid.*, **8**, 2817 (1969).
(29) F. E. Saalfield, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968).

### Table V
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR
SUBSTITUTION REACTIONS OF ML$_4$ COMPLEXES IN TOLUENE

| | CO[a] | PF$_3$[b] | P(OC$_2$H$_5$)$_3$[c] |
|---|---|---|---|
| | | M = Ni | |
| $k(25°)$, sec$^{-1}$ | $2.03 \times 10^{-2}$ | $2.06 \times 10^{-6}$ | $9.94 \times 10^{-7}$ |
| $\Delta H^*$, kcal/mol | $22.3 \pm 0.2$ | $28.4 \pm 1.1$ | $26.2 \pm 1.0$ |
| $\Delta S^*$, eu | $8.4 \pm 1$ | $10.7 \pm 1.9$ | $1.8 \pm 3.0$ |
| | | M = Pd | |
| $k(25°)$, sec$^{-1}$ | ... | ... | $2.07 \times 10^3$ |
| $\Delta H^*$, kcal/mol | ... | ... | $22.0 \pm 2.3$ |
| $\Delta S^*$, eu | ... | ... | $30.4 \pm 8.6$ |
| | | M = Pt | |
| $k(25°)$, sec$^{-1}$ | ... | $1.05 \times 10^{-1}$ | $2.60 \times 10^{-2}$ |
| $\Delta H^*$, kcal/mol | ... | $22.5 \pm 0.9$ | $27.5 \pm 1.6$ |
| $\Delta S^*$, eu | ... | $12.3 \pm 1.4$ | $26.8 \pm 4.4$ |

[a] Reference 8.  [b] This work.  [c] Reference 10.

the activation enthalpies should provide a reasonably good measure of the relative metal–ligand bond strengths.

It must also be noted that in these dissociative reactions the CO and PF$_3$ are leaving different residues; *i.e.*, CO dissociates leaving Ni(CO)$_3$ and PF$_3$ dissociates leaving Ni(PF$_3$)$_3$. It would clearly be desirable to have data in which CO and PF$_3$ leave from a common residue. In any case it appears that the assumption that carbon monoxide and phosphorus trifluoride have very similar bonding properties should be viewed with considerable caution.

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# Catalatic Activity of Metal Chelates and Mixed-Ligand Complexes in the Neutral pH Region.   III.   Copper Chelates with Bidentate and Tetradentate Amines

By V. S. SHARMA and JACK SCHUBERT*

The catalytic decomposition of hydrogen peroxide, *i.e.*, catalatic reaction, in phosphate buffer by Cu(II) chelates of ethylenediamine (en), 1,3-diaminopropane (DAP), and triethylenetetramine (TETA) has been investigated from the initial rates of O$_2$ evolution using a differential manometric technique. The rates of O$_2$ evolution are first order with respect to the 1:1 metal–ligand chelates of copper with the diamines and HOO$^-$. The chelates of DAP or histamine which form six-membered rings with Cu(II) appear more active than the five-membered chelate ring of Cu(II)–en. The four-coordinated Cu(II)–TETA complex possesses little catalatic activity. For the reaction of hydrogen peroxide with Cu(II) complexes to proceed, the data suggest that (1) the copper complex must have a suitable redox potential to facilitate electron transfer from the peroxide anion to the central metal ion and (2) the complex must possess two adjacent free sites to facilitate the reaction of the intermediate L–Cu–OOH$^+$ with a second peroxide anion.

## Introduction

In previous communications[1–3] on the kinetics of

(1) (a) J. Schubert, V. S. Sharma, E. R. White, and L. S. Bergelson, *J. Amer. Chem. Soc.*, **90**, 4476 (1968); (b) J. Schubert and V. S. Sharma, *Proc. Int. Conf. Coord. Chem., 11th*, 19–22 (1968).
(2) V. S. Sharma and J. Schubert, *J. Amer. Chem. Soc.*, **91**, 6291 (1969).
(3) V. S. Sharma, J. Schubert, H. B. Brooks, and F. Sicilio, *ibid.*, **92**, 822 (1970).

decomposition of hydrogen peroxide by copper complexes and chelates, we observed that the reaction appeared to involve a Cu(II)–Cu(I) couple. Factors controlling the oxidation–reduction potential of copper complexes, therefore, should also control the catalatic (*i.e.*, catalase-like) activity of these complexes.

Table I

Observed Rate, $R$, of Hydrogen Peroxide Decomposition by Copper–Ethylenediamine as a Function of pH, at 25° and [Phosphate Buffer] $= 0.013\ M$

| Reading no. | pH | $10^8 R$, l. mol$^{-1}$ sec$^{-1}$ | [Free Cu$^{2+}$],[a] $M$ | [Free en],[a] $M$ | [PO$_4^{3-}$],[a] $M$ | [HOO$^-$],[a] $M$ |
|---|---|---|---|---|---|---|
| 1 | 6.01 | 1.08 | $1.873 \times 10^{-5}$ | $2.127 \times 10^{-10}$ | $3.522 \times 10^{-9}$ | $8.547 \times 10^{-8}$ |
| 2 | 6.52 | 1.603 | $6.59 \times 10^{-6}$ | $3.569 \times 10^{-10}$ | $2.668 \times 10^{-8}$ | $2.762 \times 10^{-7}$ |
| 3 | 7.01 | 3.55 | $2.659 \times 10^{-6}$ | $5.006 \times 10^{-10}$ | $1.406 \times 10^{-7}$ | $8.578 \times 10^{-7}$ |
| 4 | 7.06 | 7.607 | $1.757 \times 10^{-6}$ | $5.453 \times 10^{-10}$ | $1.628 \times 10^{-7}$ | $1.916 \times 10^{-6}$ |
| 5 | 7.15 | 0.409 | $3.802 \times 10^{-9}$ | $3.962 \times 10^{-8}$ | $2.145 \times 10^{-7}$ | $1.18 \times 10^{-6}$ |
| 6 | 7.24 | 2.82 | $8.717 \times 10^{-7}$ | $5.694 \times 10^{-10}$ | $2.761 \times 10^{-7}$ | $1.449 \times 10^{-6}$ |
| 7 | 7.62 | 3.70 | $3.994 \times 10^{-7}$ | $7.111 \times 10^{-10}$ | $7.635 \times 10^{-7}$ | $3.473 \times 10^{-6}$ |
| 8 | 7.80 | 2.83 | $3.44 \times 10^{-7}$ | $7.804 \times 10^{-10}$ | $1.199 \times 10^{-6}$ | $3.151 \times 10^{-6}$ |
| 9 | 8.08 | 3.068 | $1.694 \times 10^{-7}$ | $9.723 \times 10^{-10}$ | $2.372 \times 10^{-6}$ | $5.998 \times 10^{-6}$ |

| $10^4$[Cu$^{2+}$]$_T$, $M$ | [H$_2$O$_2$]$_T$, $M$ | $10^4$[en]$_T$, $M$ | Reading no. |
|---|---|---|---|
| 5.33 | 0.0333 | 5.33 | 1, 2, 3 |
| 5.33 | 0.0667 | 5.33 | 4 |
| 5.33 | 0.0333 | 1.07 | 5 |
| 2.66 | 0.0333 | 2.66 | 6, 7 |
| 2.66 | 0.0200 | 2.66 | 8, 9 |

[a] The concentrations of these species for the conditions employed were calculated from the following constants expressed as overall stability constants (log $\beta$) as defined in the text. The constants for the species marked with an asterisk were estimated from the equations proposed in ref 9 and 10: Hen, 10.09; H$_2$en, 17.09;[10] H$_3$PO$_4$, 20.61; H$_2$PO$_4$, 18.5; HPO$_4$, 11.8;[11] H$_2$O$_2$, 11.6;[12] Cu(en), 10.67; Cu(en)$_2$, 19.9;[13] Cu(H$_2$PO$_4$), 19.25; Cu(HPO$_4$), 15.0;[11] Cu(OH), −6.5; Cu(OH)$_2$, −10.95; Cu$_3$(OH)$_4$, −22.1;[14] Cu(en)(H$_2$PO$_4$)*, 29.20; Cu(en)(HPO$_4$)*, 24.95; Cu(HOO)*, 6.45;[1] Cu(en)(HOO)*, 17.12; Cu(en)(OH), 3.67.[15]

This paper deals with the effect of the ring size of the chelate and the number of donor groups in a ligand coordinated to the central metal ion on the catalatic activity of the chelate. The ligands employed for this purpose are ethylenediamine (en), 1,3-diaminopropane (DAP), and triethylenetetramine (TETA). The former two ligands give five- and six-membered ring chelates, respectively, while TETA forms a four-coordinated copper complex. The kinetic data confirm our previous work,[1-3] which indicated that the predominantly active species are those in which two nitrogens are coordinated to the copper ion in the cis position.

## Experimental Section

**Apparatus and Procedure.**—The evolution of oxygen during the course of H$_2$O$_2$ decomposition in the presence of oxygen-saturated solutions of copper complexes was measured as a function of time with a differential syringe manometer, as described previously.[2] Because of possible secondary reactions between hydrogen peroxide and the ligands,[4] the kinetics were obtained from the initial rates of O$_2$ evolution. The observed rates of O$_2$ evolution, $R$, in microliters per second, obtained from the slopes of a plot of microliters of O$_2$ evolved vs. time, were converted to $k_{obsd}$ in the units of liters per mole per second as described previously. These rates, together with the corresponding conditions of pH, total metal, total ligand, and total H$_2$O$_2$ concentrations, are given later. Since these rates were sensitive to the concentration and nature of the buffer,[1b] all kinetic runs were made at a total phosphate buffer concentration of 0.013 $M$ and at 25°. A high H$_2$O$_2$:Cu(II) ratio was maintained since the kinetics of H$_2$O$_2$ decomposition are dependent on the relative concentrations of H$_2$O$_2$ and the metal ion.[4,5]

**Chemicals.**—Technical grade ethylenediamine, 1,3-diaminopropane, and triethylenetetramine were purified by double distillation. Their standard solutions were prepared by volumetric titration in the presence of bromophenol blue as an indicator.[6]

All other reagents were prepared as described earlier.[2] The pH of the solutions was checked with an ORION digital pH meter using 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°, as standards. No attempt was made to convert hydrogen ion activity into concentration. No visible precipitate or turbidity was observed in solutions over the time period of kinetic runs.

**Tests for Cuprous Ion.**—The formation of the cuprous state in copper(II)–amine–hydrogen peroxide solutions was tested with 2,2'-biquinoline which produces a pink color characteristic of the copper(I)–biquinoline complex.[7]

**Chemical Test for OH Radical.**—The polymerization of acrylonitrile was employed[4,5] to detect free radical formation. No polymerization was observed in any of the solutions despite precautions to exclude oxygen from the system. Kinetic runs in the presence of 5% of methyl alcohol, an OH scavenger, gave rates of O$_2$ evolution similar to those obtained in the absence of the scavenger.

## Results and Discussion

**Solution Equilibria.**—In aqueous solutions containing copper ion and ligand (en or DAP) in phosphate buffer, the following equilibria are considered: (a) ionization of the ligand and formation of the 1:1 and 1:2 copper–amine complexes, (b) ionization of hydrogen peroxide and the formation of a Cu(OOH)$^+$ complex, (c) ionization of H$_3$PO$_4$ into H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$, (d) the formation of copper complexes of H$_2$PO$_4^-$ and HPO$_4^{2-}$, (e) hydrolysis of copper(II) ions to give Cu(OH)$^+$, Cu$_2$(OH)$_2^{2+}$, and Cu$_3$(OH)$_4^{2+}$, (f) formation of mixed complexes of amines, phosphoric acid, and hydrogen peroxide with copper, and (g) formation of hydrolyzed species of copper–amine complexes, LCuOH$^+$. In all, we have taken into account the formation of 18 species existing in dynamic equilibrium with each other. The equilibrium concentrations of the various species were calculated on an IBM 360/50 computer by an iterative procedure from expressions for total metal, total ligand,

(4) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **51**, 935 (1955).

(5) (a) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *ibid.*, **47**, 462 (1951); (b) *ibid.*, **47**, 591 (1951).

(6) J. Rosin, "Reagent Chemicals and Standards," 2nd ed, Van Nostrand, New York, N. Y., 1955, p 182.

(7) I. M. Klotz and T. A. Klotz, *Science*, **121**, 477 (1955).

Table II

OBSERVED RATE, $R$, OF HYDROGEN PEROXIDE DECOMPOSITION BY COPPER-1,3-DIAMINOPROPANE AS A

FUNCTION OF pH, at 25°, $[Cu^{2+}]_T = 1.33 \times 10^{-4} M$, $[DAP]_T = 2.66 \times 10^{-4} M$,

$[H_2O_2]_T = 0.0333 M$, AND $[PHOSPHATE BUFFER]_T = 0.013 M$

| pH | $10^8 R$, l. mol$^{-1}$ sec$^{-1}$ | $[Cu^{2+}]$,$^a$ $M$ | $[DAP]$,$^a$ $M$ | $[PO_4{}^{3-}]$,$^a$ $M$ | $[HOO^-]$,$^a$ $M$ |
|---|---|---|---|---|---|
| 7.05 | 1.00 | $3.552 \times 10^{-6}$ | $5.187 \times 10^{-10}$ | $1.591 \times 10^{-7}$ | $9.374 \times 10^{-7}$ |
| 7.36 | 1.84 | $1.096 \times 10^{-6}$ | $1.699 \times 10^{-9}$ | $3.864 \times 10^{-7}$ | $1.912 \times 10^{-6}$ |
| 7.49 | 2.66 | $5.785 \times 10^{-7}$ | $2.892 \times 10^{-9}$ | $5.470 \times 10^{-7}$ | $2.579 \times 10^{-6}$ |
| 7.69 | 2.76 | $1.883 \times 10^{-7}$ | $6.424 \times 10^{-9}$ | $9.147 \times 10^{-7}$ | $4.086 \times 10^{-6}$ |
| 7.85 | 3.11 | $7.067 \times 10^{-8}$ | $1.268 \times 10^{-8}$ | $1.361 \times 10^{-6}$ | $5.905 \times 10^{-6}$ |

$^a$ The concentrations of these species for the equilibrium conditions employed were calculated from the following constants expressed as log $\beta_i$ (overall stability constant).[2] The constants marked with an asterisk were calculated from equations proposed in ref 9 and 10: H(DAP), 10.72;[16] H$_2$(DAP), 19.70; Cu(DAP), 9.77; Cu(DAP)$_2$, 16.94;[16] Cu(H$_2$PO$_4$)(DAP)*, 27.72; Cu(HPO$_4$)(DAP)*, 23.47; Cu(HOO)(DAP)*, 16.22; Cu(DAP)(OH)*, 2.67; other constants are the same as listed in footnote $a$ to Table I.

total phosphate, and total peroxide concentrations.[8] A listing of these species together with the logarithms of their overall stability constants, obtained from the literature as cited, is given in the footnotes to Tables I and II.[9-16]

The overall practical constants are defined as $\beta = [M_m A_a B_b (H^+ \text{ or } OH^-)_w]/[M]^m[A]^a[B]^b[OH^- \text{ or } H^+]^w$, where M, A, B represent, respectively, metal ion, ligand A, and ligand B, while $m$, $a$, $b$, and $w$ are positive integers or zero. From the knowledge of the stability constants, pH, and free ligand (en or DAP, PO$_4{}^{3-}$, HOO$^-$) and free metal ion concentrations, the concentration of any species listed in the footnotes to Tables I and II can be calculated. The concentrations of Cu(en)$_2{}^{2+}$, Cu(en)$^{2+}$, enCu(OH)$^+$, Cu$^{2+}$, and HOO$^-$ as a function of pH are plotted in Figure 1. The constant for the hydrolyzed species (DAP)Cu(OH)$^+$ was assumed to be the same as for enCu(OH)$^+$. This is justified in view of the fact that the p$K_a$ for the equilibrium LCu$^{2+} \rightleftarrows$ LCu(OH)$^+$ + H$^+$ is relatively unaffected by the nature of the ligand.[15] It should be noted that the values 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 Data.**—While the differential method employed gave a measure of the net O$_2$ evolved relative to the copper-free controls, experiments were carried out to determine the degree to which all conceivable combinations of the solution components decomposed H$_2$O$_2$. The only combinations which gave significant volumes of O$_2$ at the concentrations and pH's employed were those which contained copper, amine, and H$_2$O$_2$. Therefore, nonamine-containing species of copper, uncomplexed amine, and various ionized and un-ionized buffer (H$_3$PO$_4$, H$_2$PO$_4{}^-$, HPO$_4{}^{2-}$, PO$_4{}^{3-}$, etc.) species need not be considered in the derivation of the rate equation.

(8) D. D. Perrin and V. S. Sharma, *J. Inorg. Nucl. Chem.*, **28**, 2171 (1966).

(9) V. S. Sharma and J. Schubert, *J. Chem. Educ.*, **46**, 506 (1969).

(10) Y. Kanemura and J. I. Watters, *J. Inorg. Nucl. Chem.*, **29**, 1701 (1967).

(11) G. Schwarzenbach and G. Geir, *Helv. Chim. Acta*, **46**, 906 (1963).

(12) M. G. Evans and N. Uri, *Trans. Faraday Soc.*, **45**, 224 (1949).

(13) C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, **62**, 444 (1958).

(14) D. D. Perrin, *J. Chem. Soc.*, 3189 (1960).

(15) R. C. Courtney, R. L. Gustafson, S. Chaberek, and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 519 (1959).

(16) L. G. Sillén and A. E. Martell, "Tables of Stability Constants of Metal Complexes," 2nd ed, The Chemical Society, London, 1965.
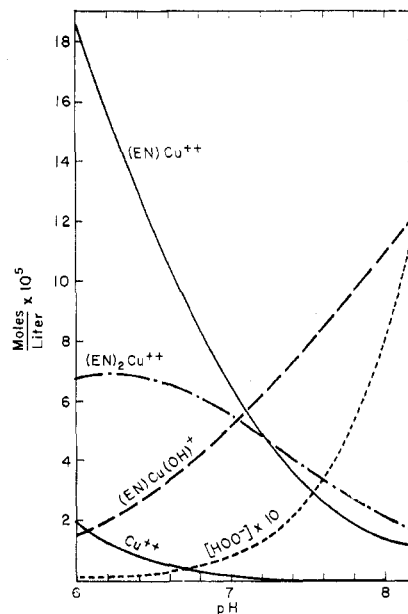


Figure 1.—Concentrations of enCu$^{2+}$, (en)$_2$Cu$^{2+}$, enCu(OH)$^+$, Cu$^{2+}$, and HOO$^-$ as functions of pH. $[Cu^{2+}]_T = 0.533 \times 10^{-3} M$; $[en]_T = 0.533 \times 10^{-3} M$; $[H_2O_2]_T = 0.0333 M$; [sodium phosphate buffer]$_T = 0.013 M$. Not all of the copper-containing species are included. See Table I for a complete listing.

For reasons such as reduced charge and free coordinating sites on the complex species,[17] the four-coordinated 1:2 copper–amine complexes and the mixed complexes of copper with en or DAP and H$_2$PO$_4{}^-$ and HPO$_4{}^{2-}$ can also be ignored in the rate equation.[1-3] The remaining complex species, therefore, which may contribute toward O$_2$ evolution are CuL$^{2+}$ and LCu(OH)$^+$.

In all essentials, copper complexes of ethylenediamine and 1,3-diaminopropane behaved in similar manners. However, because of the weaker complexing ability of 1,3-diaminopropane, a twofold excess of ligand was required to keep solutions clear and to form CuL$^{2+}$ in concentrations sufficient to give measurable rates of hydrogen peroxide decomposition. This increased the possibility that free 1,3-diaminopropane would react directly with hydrogen peroxide. It is presumably for this reason that the initial linear portions of O$_2$ evolved vs. time plots were much shorter for this system. At higher pH, they become still shorter, and, therefore,

(17) (a) J. H. Wang, *J. Amer. Chem. Soc.*, **77**, 4715 (1955); (b) H. Sigel, *Angew. Chem.*, **8**, 167 (1969).

studies for this system could not be carried out beyond pH 7.8.

**Copper–Ethylenediamine System.**—The dependence of the rate of $O_2$ evolution on the concentration of various species was investigated by keeping the total concentration of all but one of the components constant. In a dynamic equilibrium condition, however, this procedure was accompanied by some changes in the concentration of all other reactive species also. To take into account the latter factor, the dependence of $R/[Cu^{2+}] \cdot [HOO^-]$, $R/[en][HOO^-]$, or $R/[HOO^-]$ on $[en]$, $[Cu^{2+}]$, and $[ML^{2+}]$, respectively, was investigated. At constant pH, a more than tenfold variation in total $H_2O_2$ concentration revealed that the rate of $O_2$ evolution was first order in $H_2O_2$ concentration. The effect of pH on the rates of hydrogen peroxide decomposition is shown in Figure 2. The lines in Figure 2, if extrap-
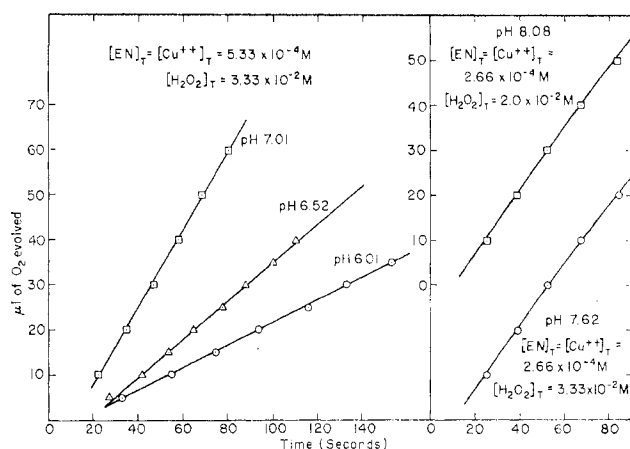


Figure 2.—The effect of pH on the rate of hydrogen peroxide decomposition by copper–ethylenediamine at 25° and [phosphate buffer] = 0.013 $M$. In order to avoid overlapping with the curve at pH 7.62, the $y$ axis for the curve at pH 8.08 has been raised by 40 $\mu$l.

olated, do not pass through the origin. This is, in part, due to factors such as an error in the zero-time reading, incomplete mixing of $H_2O_2$ solution into the chelate solution, and the presence of an *induction period*. With the manometric technique it was not possible to obtain readings below 20 sec and therefore a few kinetic runs were made on an automatic precision pressure gauge capable of taking readings at 0.5-sec intervals. These runs showed that the rate of $O_2$ evolution is slow at first.

The dependence of the rate of $O_2$ evolution with respect to $[ML^{2+}]$ was investigated first, by maintaining the pH and total $H_2O_2$ and total copper concentrations constant while varying the ligand concentration. In a second set of experiments, the total ligand concentration was kept constant while the total copper concentration was varied. At constant pH and $[H_2O_2]_T$, when the total ligand concentration was varied fourfold, *i.e.*, $0.266 \times 10^{-3}$–$0.107 \times 10^{-2}$ $M$, the free ligand concentration increased 660-fold from $6.027 \times 10^{-11}$ to $3.962 \times 10^{-8}$ $M$, and $[ML^{2+}]$ varied tenfold, *i.e.*, $7.0 \times 10^{-6}$–$6.9 \times 10^{-5}$ $M$. In these experiments the rate was observed to be first power in $[ML^{2+}]$ (Figure 3).
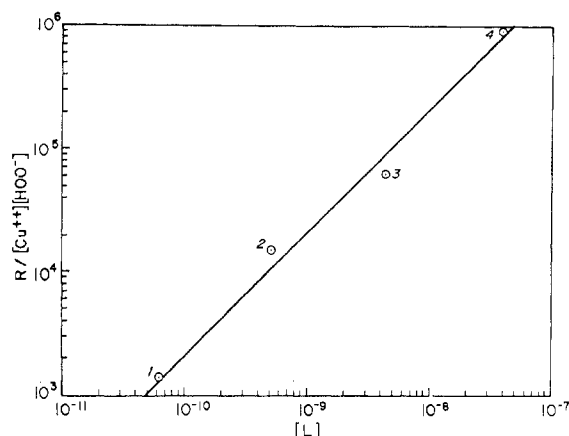


Figure 3.—First-order dependence of rate of hydrogen peroxide decomposition on free ethylenediamine concentration at 25°. $[Cu^{2+}]_T = 5.33 \times 10^{-4}$ $M$; $[H_2O_2]_T = 0.0333$ $M$; [phosphate buffer]$_T = 0.013$ $M$. Values for $[en]_T$ $(M)$ and pH are as follows for the points on the figure: (1) $1.07 \times 10^{-3}$, 7.15; (2) $0.800 \times 10^{-3}$, 7.10; (3) $0.533 \times 10^{-3}$, 7.05; (4) $0.266 \times 10^{-3}$, 7.04.

When pH and total ligand and peroxide concentrations were kept constant while the total copper was varied 20-fold in the range $0.533 \times 10^{-3}$–$0.266 \times 10^{-4}$ $M$, the free copper and $ML^{2+}$ concentrations changed from $1.7 \times 10^{-6}$ to $2.668 \times 10^{-9}$ and from $1.3 \times 10^{-5}$ to $1.0 \times 10^{-6}$ $M$, respectively. In these runs, also, the rate was first order in $[ML^{2+}]$.

The rate studies at constant pH, however, cannot be used to resolve the relative contributions of $[ML^{2+}]$ or $[ML(OH)^+]$ in the rate expression because at constant pH, the ratio $[ML(OH)^+]/[ML^{2+}]$ is also constant. Further, at constant pH, the data do not provide a basis for determining whether $HOO^-$ or $H_2O_2$ are the reactive species. The rate of $O_2$ evolution was, therefore, measured as a function of pH. In the pH range 6–8, $[HOO^-]$, $[ML^{2+}]$, and $[ML(OH)^+]$ change by factors of 70, 23.4, and 5, respectively; nor was the ratio $[ML(OH)^+]/[ML^{2+}]$ constant. A plot of $R/[ML^{2+}]$ *vs.* $[HOO^-]$ gave a straight line passing through
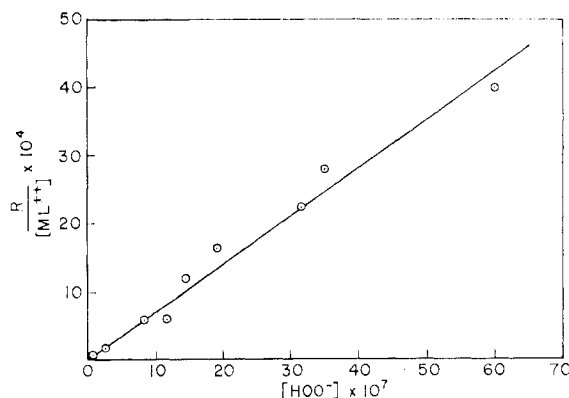


Figure 4.—Graphical evaluation of rate constant $k_1$ for hydrogen peroxide decomposition by the $Cu^{II}en^{2+}$ chelate, at 25°. Initial total concentrations $[Cu^{2+}]_T$, $[en]_T$, $[H_2O_2]_T$, and [phosphate buffer]$_T$ are the same as in Table I.

the origin (Figure 4). These observations fit the rate expression

$$R = k_1[CuL^{2+}][HOO^-] \tag{1}$$
$$= k_1\beta_{11}[Cu^{2+}][L][HOO^-] \tag{2}$$

These equations, in agreement with the kinetic data, assume that the hydrolyzed species $LM(OH)^+$ is catalytically inactive. However, in view of the fact that in the copper–imidazole system the $(L)_2Cu(OH)^+$ species appeared to be slightly active, the possible activity ($<10\%$ of the overall reaction rate) of $LCu(OH)^+$ should not be ruled out. The apparent rate constant, $k_1$, as obtained from the slope of the straight line in Figure 4, is 700 l. $mol^{-1}$ $sec^{-1}$ for the copper–ethylenediamine system.

**Copper–1,3-Diaminopropane System.**—The copper–1,3-diaminopropane system behaves toward $H_2O_2$ in a manner similar to that of the copper–ethylenediamine system. However, as mentioned earlier, this system could be studied only in the pH range 7–7.8. The apparent rate constant as calculated from the slope of the straight line obtained by plotting $R/[ML^{2+}]$ vs. $[HOO^-]$ is 1000 l. $mol^{-1}$ $sec^{-1}$. The values of the apparent rate constants reported here for Cu–en and Cu–DAP systems are relevant only to the present experimental conditions and depend on the values of the stability constants chosen for calculating the concentrations of the various species.
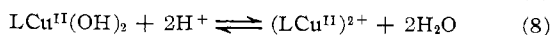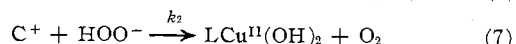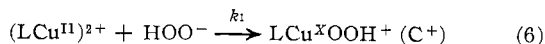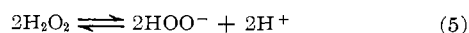
**Triethylenetetramine System.**—TETA gives four-coordinated copper complexes. As expected, since no free coordinating sites are available, the TETA–$Cu^{II}$ chelate was found to be inactive. The biquinoline test for the presence of Cu(I) ions proved negative, and no oxygen was evolved, even after 60 min of reaction time.

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

$$R = k_2[LCu^{II}HOO^+] \qquad (3)$$

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

It is not possible to decide from kinetic data alone whether the reaction proceeds by either one or both of these steps since in terms of concentrations of the free ligand, peroxide anion, and free metal, both sets of equations ((1) and (3)) are equivalent and differ only with respect to the formation constants of $ML^{2+}$ and mixed-ligand complex species, $LMOOH^+$. One can explain the kinetic data and obtain eq 1 and 2 by assuming the sequence of reactions

$$2H_2O_2 \rightleftharpoons 2HOO^- + 2H^+ \qquad (5)$$

$$(LCu^{II})^{2+} + HOO^- \xrightarrow{k_1} LCu^xOOH^+ (C^+) \qquad (6)$$

$$C^+ + HOO^- \xrightarrow{k_2} LCu^{II}(OH)_2 + O_2 \qquad (7)$$

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

Later in the discussion, it is pointed out that the rate-determining step is reaction 6 (*i.e.*, $k_2 > k_1$). Therefore, at the end of the induction period the steady-state concentration of $C^+$ can be written
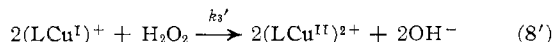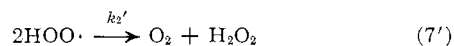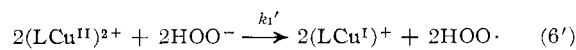
$$d(C^+)/dt = 0 = k_1[(LCu^{II})^{2+}][HOO^-] - k_2[C^+][HOO^-]$$

therefore

$$R = d(O_2)/dt = k_1[(LCu^{II})^{2+}][HOO^-] \qquad (9)$$

which is the same as eq 1.

The intermediate $C^+$ can be considered as the mixed-ligand chelate of copper(II) with the ligand L and peroxide anion $HOO^-$. The mechanism in this case, therefore, will be the same as the one proposed by Wang[17a] for the decomposition of $H_2O_2$ by Fe(III) complexes. However, Wang's mechanism assumes that the peroxide anion is bidentate, for which there is no direct evidence. Alternatively, therefore, the intermediate $C^+$ might be considered as the complex of copper(I) with ligand L and HOO free radical, and the mechanism on this assumption is similar to that proposed by Barb, *et al.*, for the iron(III)–2,2'-bipyridyl system.[4] The failure to detect radical intermediates by esr has been attributed to their extremely small concentrations at any time during the reaction.[3] However, in view of the negative tests for the OH radical, any mechanism involving free radicals should postulate the formation of the HOO radical only. From these considerations, for example, one can write the reaction scheme suggested by a referee

$$2(LCu^{II})^{2+} + 2HOO^- \xrightarrow{k_1'} 2(LCu^I)^+ + 2HOO\cdot \qquad (6')$$

$$2HOO\cdot \xrightarrow{k_2'} O_2 + H_2O_2 \qquad (7')$$

$$2(LCu^I)^+ + H_2O_2 \xrightarrow{k_3'} 2(LCu^{II})^{2+} + 2OH^- \qquad (8')$$

In terms of the rate of oxygen evolution, reaction scheme (6')–(8') will also give the same rate law as the reaction scheme (6)–(8), provided a steady-state approximation is made for the radical $HOO\cdot$.
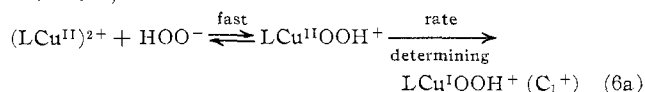
The formation of the cuprous ion was demonstrated by the 2,2'-biquinoline test. In the absence of chelating amines at pH 6.01 under the experimental conditions listed in Table I there was no development of pink color for 30 min after the addition of 2,2'-biquinoline, nor was there any significant evolution of oxygen. However, in the presence of chelating amines it took less than 10 sec to develop the color accompanied by $O_2$ evolution. These observations indicate that, as compared to aquocupric ion, the reduction of Cu(II) coordinated to two nitrogens is kinetically much faster and that the Cu(I) state of the complex is involved in the catalytic decomposition of hydrogen peroxide. The formation of the Cu(I) state, therefore, suggests that the free radical $HOO\cdot$ is presumably formed *within* the coordination sphere of the metal ion[18] in very small concentrations undetectable by esr.

A third alternative is to regard the intermediate $C^+$ as being in the "entatic,"[19] *i.e.*, reactive transition state, which is attained with equal ease by the conventional stable cupric and cuprous forms of the intermediate during its reversible oxidation–reduction, where the description of the complex as either cuprous or cupric is meaningless. In the presence of Cu(I)-selective ligands such as 2,2'-biquinoline the intermediate $C^+$ could easily acquire the conventional cuprous form of the complex.

(18) H. Sigel, C. Flierl, and R. Griesser, *J. Amer. Chem. Soc.*, **91**, 1061 (1969).

(19) B. L. Vallee and R. J. P. Williams, *Proc. Nat. Acad. Sci. U. S.*, **59**, 498 (1968).

In spite of these uncertainties regarding the exact nature of the intermediate $C^+$ there is little doubt that the peroxide entity in it becomes highly reactive.[4,5,17a] This is presumably due to the polarization of the peroxide anion (in the intermediate $C^+$) by the dipositive metal chelate $LM^{2+}$, due to the creation of electron-deficient oxygen as explained by Wang,[17a] or simply due to the formation of HOO· free radical[18] within the coordination sphere of the metal ion. These considerations indicate that the rate-determining step is reaction 6. In view of the lability of $Cu^{II}$,[20] it seems that the formation of the mixed-ligand complex $LCu^{II}OOH^+$ $(LCu^{II}(H_2O)_2^{2+} + HOO^- \rightleftharpoons LCu^{II}(H_2O)OOH^+ + H_2O)$ is fast, and therefore the rate-determining step most probably involves the electron transfer from the peroxide anion to the chelate $(LCu^{II})^{2+}$. Step 6 can, therefore, be written as

$$(LCu^{II})^{2+} + HOO^- \underset{fast}{\rightleftharpoons} LCu^{II}OOH^+ \xrightarrow[\text{determining}]{\text{rate}}$$
$$LCu^IOOH^+ \ (C_1^+) \quad (6a)$$

In Table III are listed the apparent rate constants

TABLE III

APPARENT RATE CONSTANTS FOR THE DECOMPOSITION OF HYDROGEN PEROXIDE BY COPPER COMPLEXES AT 25° AND IN 0.013 $M$ SODIUM PHOSPHATE BUFFER

| Species | App rate constant, $k$, l. mol$^{-1}$ sec$^{-1}$ | Ref |
|---|---|---|
| Cu(imidazole)$^{2+}$ | Inactive | a |
| Cu(imidazole)$_2^{2+}$ | 530 | a |
| Cu(imidazole)$_3^{2+}$ | Inactive | a |
| Cu(en)$^{2+}$ | 700 | b |
| Cu(DAP)$^{2+}$ | 1000 | b |
| Cu(histamine)$^{2+}$ | 1300 | c |
| Cu(histidine)$^+$ | 130 | d |
| Cu(TETA)$^{2+}$ | Inactive | b |

[a] Reference 2. [b] Present paper. [c] J. Schubert and V. S. Sharma, unpublished work. [d] Reference 3.

for the decomposition of hydrogen peroxide by copper complexes under identical conditions. The values listed lead to the following conclusions. (1) Complexes of anionic ligands (copper–histidine) are much less active as compared to the corresponding complexes of neutral ligands.[17a] (2) Complexes having less than two free sites on the metal ion are inactive (Cu(TETA), Cu(imidazole)$_3$). This observation is presumably related to the bidentate nature of peroxide

(20) A. F. Pearlmutter and J. Stuehr, *J. Amer. Chem. Soc.*, **90**, 858 (1968).

anion or to the fact that the remaining fourth free position on the intermediate $C^+$ will facilitate its reaction with the second peroxide anion. (3) Although the rate constants for two-nitrogen-coordinated copper species do not vary much despite wide differences in the nature of ligands and the stabilities of the corresponding copper complexes, there appears to be a *trend* toward higher catalatic activity on increasing the ring size of the chelate (Cu(en), Cu(DAP), and copper–histamine).

The above observations can be qualitatively explained by redox potential considerations of copper complexes.[2,3] The redox potential of copper complexes having two nitrogen donors is optimum[21] for a one-electron transfer from the peroxide anion to the central metal ion. Thus, the standard potential of the Cu(II)–Cu(I) couple in water of $+167$ mV becomes more positive by about $+90$ mV for each nitrogen as the water molecules are replaced by up to two nitrogen atoms.[21] However, the reduction potential becomes less positive for three or more coordinated nitrogen atoms because of the preference of cuprous ions to be only two-coordinate and linear with saturated nitrogen ligands while cupric ions may become at least four-coordinate.[2,3]

The high stability and rigid structure of the (TETA–$Cu^{II})^{2+}$ complex does not allow the structural changes demanded by the Cu(I) ion, nor does it have any free site on it to form the postulated intermediate L–M–OOH$^+$. As a result, the Cu–TETA chelate is inactive.

The somewhat higher activity of the six-membered ring chelate is probably related to the greater ease with which it can remain coordinated to both cuprous and cupric forms of the metal ion during its reversible oxidation–reduction. Ethylenediamine, on the other hand, will retain a chelate structure in the tetrahedral Cu(I) complex only under great strain, or alternatively it must become monodentate before resuming a bidentate structure in the cupric form of the complex.[22] In either case, its catalytic activity would be expected to be lower than that of the DAP–Cu$^{II}$ and histamine–Cu$^{II}$ species.

(21) A. S. Brill, R. B. Martin, and R. J. Williams, *Electron. Aspects Biochem., Proc. Int. Symp., 1963*, 519–557 (1964).
(22) C. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, 1351 (1962).