# Nature and Mechanism of Decomposition of the Complex of Copper(I) with 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene in Aqueous Solutions. A Pulse Radiolytic Study

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The reduction of $Cu^{II}L$ in water by hydrated electrons $\cdot CH_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$ were studied. The planar $Cu^{I}L$ formed is transformed in neutral or slightly acidic solutions to $Cu^{III}L-H$. $Cu^{I}L$(planar) and $Cu^{III}L-H$ are in equilibrium with another form of $Cu^{I}L$ plausibly with a tetrahedral configuration. The latter form is stable in neutral and alkaline solutions and is identical with the $Cu^{I}L$ formed electrochemically. In acidic solutions, pH <5.5, $Cu^{I}L$ decomposes to Cu^+ + LH_2^{2+} in an acid-catalyzed process.

The search for compounds which might photocatalyze the photolytic decomposition of water to yield hydrogen stirred us to reinvestigate the mechanism of reduction of $Cu^{II}L$ (where L ≡ 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).

L
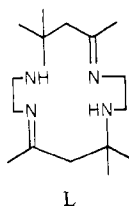
It was suggested[1] that $Cu^{I}L$ reacts with acid according to the reaction
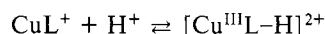
$$CuL^+ + H^+ \rightleftarrows [Cu^{III}L-H]^{2+}$$

It was hoped that this reaction is followed in acid solutions by the reaction

$$[Cu^{III}L-H]^{2+} + H^+ \rightarrow Cu^{III}L + H_2$$
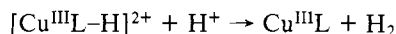
as was reported for several hydrido complexes.[2] The results obtained in the present study indicate that though $[Cu^{III}L-H]^{2+}$ is formed in this system, it decomposes into Cu^+ + LH_2^{2+}. However the results help in clarifying the detailed mechanism of reduction of $Cu^{II}L$, which was not studied in detail in the past, and indicate that the stable CuL^+ formed in deaerated neutral and alkaline solutions has a tetrahedral and not planar configuration.

Experimental Section

(a) Materials. $Cu^{II}L(ClO_4)_2$ was prepared as described in the literature[3] by the reaction of $Cu(O_2CCH_3)_2$ with (*trans*-[14]diene)·2HClO$_4$ in methanol. The UV–visible spectrum of the complex was identical with that reported in the literature.[3] All other chemicals used were AR grade and were used without any further purification. No attempt to keep constant ionic strength was made. As dilute salt solutions were used, the ionic strength range was $(1.3-3.4) \times 10^{-3}$ except for the solutions containing NaBr or HCO$_2$Na. The water used was either triple-distilled or deionized water obtained from a Millipore milli-Q setup. The N$_2$O and Ar used were bubbled through two washing bottles containing VSO$_4$ in dilute H$_2$SO$_4$ over Zn amalgam, followed by a washing bottle containing NaOH and one with triple-distilled water; thus all traces of oxygen were eliminated. pH adjustment was done by HClO$_4$ proanalysis or NaOH AR grade both supplied by Merck.

(b) Irradiation. The pulse radiolytic setup at the Hebrew University of Jerusalem was used. Electron pulses of 0.1–1.5 μs, 200 mA, and 5 MeV were used. The dose per pulse was 100–3000 rd.

Table I. Rates of Reaction Observed in Argon-Saturated Solutions^a

rate const	aliphatic solute		
	$(CH_3)_3COH$	CH_3OH	$(CH_3)_2CHOH$
k_3, s^{-1} ^{c}	$(1.5 \pm 0.2) \times 10^5$	$(1.5 \pm 0.2) \times 10^5$	2×10^5
$k_{4,5}$, s^{-1}	$(7.0 \pm 1.0) \times 10^2$	$(5.0 \pm 1.0) \times 10^2$	$(5.0 \pm 1.0) \times 10^2$
k_9,^{b} M^{-1} s^{-1}	$(6 \pm 1) \times 10^6$	$(6 \pm 1) \times 10^6$	$(5 \pm 1) \times 10^6$

^{a} k_3, k_4, and k_9 are the rates of the corresponding reactions; see text. ^{b} pH range of solutions studied between 5.5 and 4. ^{c} Rate at pH 6.0.

The irradiation cell was 4 cm long, and the analyzing light of a 150-W Xe lamp was passed three times through the cell.

The experimental setup in Jerusalem and the method used for evaluating the results, which has recently been improved by adding a capacity of on-line computer analysis, have been described in detail elsewhere.[4]

A syringe technique was employed for deaerating the aqueous solutions and filling the irradiation cell.[5]

The conductivity studies were carried out at the Van de Graaff generator at the Hahn Meitner Institute in Berlin. Pulses of 1.6-MeV electrons, 25 mA, and 0.5–5 μs were used. The dose per pulse was 150–1500 rd. The procedure and the equipment used were described earlier in detail.[6] Spectrophotometric measurements on the same solutions were carried out by using also the equipment at the Hahn Meitner Institute. In all cases the results in Berlin and Jerusalem were identical.

Results

When argon-saturated solutions containing $(1-8) \times 10^{-4}$ M $Cu^{II}L(ClO_4)_2$, 0.1–1 M *tert*-butyl alcohol, and 1.10^{-3} M phosphate buffer are irradiated, the formation of unstable intermediates with absorption bands in the visible and near-UV regions is observed. The absorption spectra of these intermediates at different times after the pulse at pH 6.0 are plotted in Figure 1.

In solutions at pH <5.5 three consecutive reactions are observed after the reaction of e_{aq}^- + $Cu^{II}L$ is over[1] (see insert Figure 1). The intermediate formed in the latter reaction has a maximum of absorption at 415 nm (Figure 1). The first of these reactions obeys a first-order rate law, the reaction rate being independent of $Cu^{II}L$ concentration but depending slightly on $[H_3O^+]$ (Figure 2). In the absence of phosphate

(1) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934.
(2) Meyerstein D. *Acc. Chem. Res.* **1978**, *11*, 43 and references therein.
(3) (a) Curtis, N. F.; Hay, R. W. *Chem. Commun.* **1966**, 524. (b) Palmer, J. M.; Papaconstantinou, E.; Endicott, J. F. *Inorg. Chem.* **1969**, *8*, 1516.
(4) Ilan, Y. Ph.D. Thesis, Hebrew University, Jerusalem, 1977.
(5) Senvar, C.; Hart, E. J. *Proc. Int. Conf. Peaceful Uses At. Energy, 2nd* **1958**, *29*, 19.
(6) Kelm, M.; Lilie, J.; Henglein, A.; Janate, E. *J. Phys. Chem.* **1974**, *78*, 882.

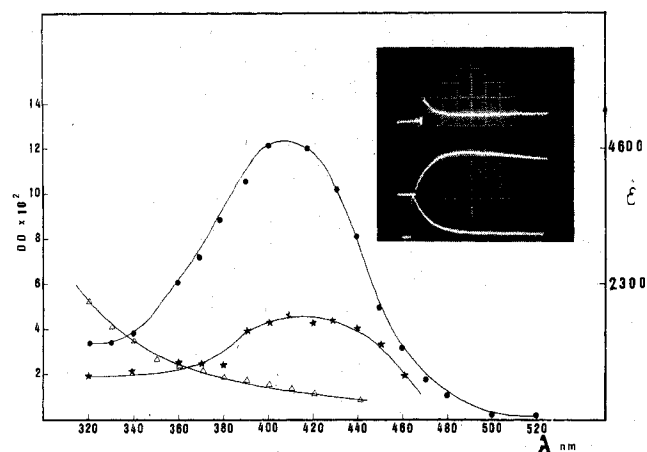*To whom correspondence should be addressed at Ben-Gurion University of the Negev.

Figure 1. Spectra of the intermediates observed in argon-saturated solutions containing 3×10^{-4} M Cu^{II}L, 0.1 M *tert*-butyl alcohol, and 1×10^{-3} M phosphate (pH 6.0 ± 0.1): ★, 1 μs after the pulse; $\triangle$, 30 μs after the pulse; ●, 8 ms after the pulse. Insert shows oscillogram traces in identical solutions but with pH 5.4 [ordinate 50 mV/div, total light signal 800 mV, and abscissa 10 μs/div (upper trace), 1 ms/div (middle trace), and 50 ms/div (lower trace)].
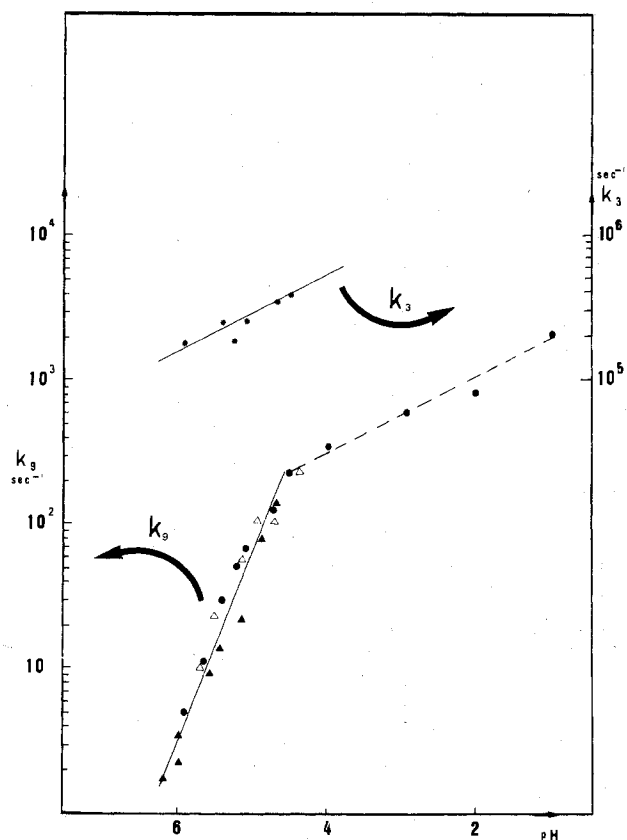

Figure 2. pH effect on k_3 and k_9; see text.

Figure 3. $\Delta\Lambda$ as a function of time (Ar-saturated solutions containing 1.9×10^{-4} M Cu^{II}L and 0.1 M 2-propanol): upper trace, pH 5.0; middle trace, pH 5.0; lower trace, pH 4.2.

buffer the value of the intercept of the plot of k_3 vs. [H$_3$O$^+$], k_3([H$_3$O$^+$] = 0) = 1.5×10^5 s^{-1}, decreases considerably, and the exact value cannot be determined as under these conditions the pH changes during the reaction. The intermediate formed in this reaction has an absorption band in the near-UV and little absorption, if any, at 410 nm (Figure 1). With use of the conductivity technique, in the absence of buffer, it is found that this reaction causes a decrease of the specific conducitivity to its value prior to the pulse (Figure 3).

The following reaction, reaction 4 below, forms an intermediate which has a maximum of absorption at 400 nm (Figure 1). This reaction obeys a first-order rate law (Table
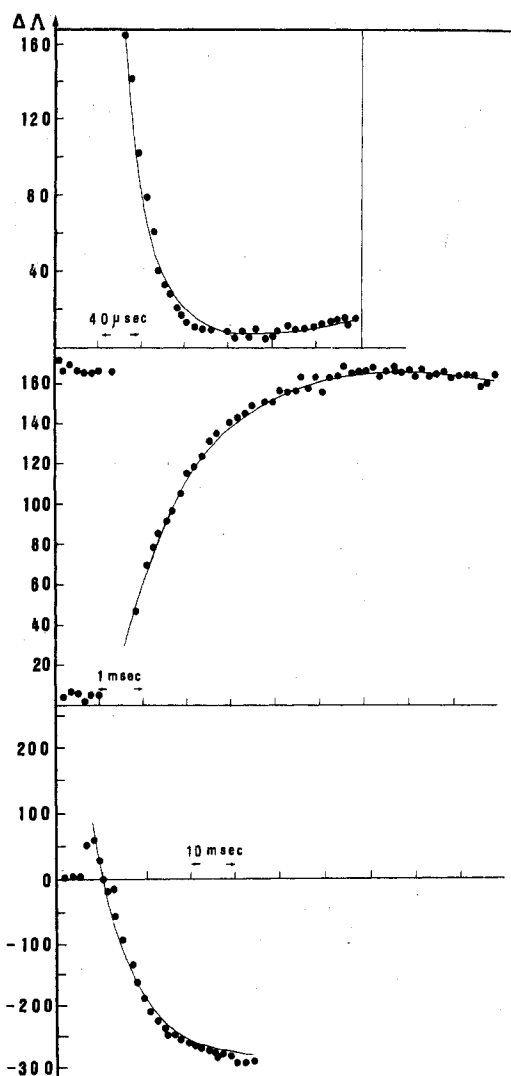
I), the rate being independent of Cu^{II}L concentration, H$_3$O$^+$ (pH 5–10 range), and pulse intensity. This reaction at pH 5.0 is accompanied by an increase, with identical kinetics, in specific conductivity of $\sim$160 cm^2 Ω^{-1} mol^{-1} (Figure 3).

The third reaction observed causes the disappearance of any absorbance at λ >320 nm. This reaction obeys a pseudo-first-order rate law, and its rate is independent of Cu^{II}L concentration and pulse intensity. This reaction is accompanied by a decrease in the specific conductivity to $\sim$−380 Ω^{-1} cm^{-1} M^{-1} relative to the value prior to the pulse (Figure 3). (Measurements at pH 2.5–5.0 were carried out.) The dependence of the rate, k_9, on [H$_3$O$^+$] is plotted in Figure 2. In the pH range of 5.0–6.0 it was found that the rate of this reaction depends also on the phosphate buffer concentration. At pH 5.9 a rate of 1.7×10^3 [H$_2$PO$_4^-$] s^{-1} for this reaction was measured. (However due to the low rate, the possibility that it is due to impurities in the phosphate cannot be absolutely ruled out.)

At pH >7 the third reaction is not observed, and the product with the strong absorption band at 400 nm seems to be stable (at least for several minutes). In the pH range of 5.5–7.0 a slight decay of absorption at 410 nm is observed during the first seconds. This decay is attributed to reactions with oxidizing impurities present, e.g., H$_2$O$_2$ formed by the pulse. The remaining absorption is stable for over 1 min.

Table II. Reactions of Primary Free Radicals with Solutes Used in This Study

reaction	k, M^{-1} s^{-1}	ref
$e_{aq}^- + N_2O \xrightarrow{H^+} N_2 + OH$	8.7×10^9	14
$e_{aq}^- + H_3O^+(aq) \rightarrow H$	2.2×10^{10}	14
$e_{aq}^- + Cu^{II}L \rightarrow Cu^IL$	5×10^{10}	1
$e_{aq}^- + $ alcohols $\rightarrow$ products	$<5 \times 10^5$	14
$OH + CH_3OH \rightarrow \cdot CH_2OH + H_2O$	7×10^8	15
$H + CH_3OH \rightarrow \cdot CH_2OH + H_2$	1.6×10^6	16
$OH + CH_3CH_2OH$	1.7×10^9	15
$\xrightarrow{87\%} CH_3\dot{C}HOH + H_2O$		
$\xrightarrow{13\%} \cdot CH_2CH_2OH + H_2O$		
$H + CH_3CH_2OH$	2.5×10^7	16
$\xrightarrow{94\%} CH_3\dot{C}HOH + H_2$		
$\xrightarrow{6\%} \cdot CH_2CH_2OH + H_2$		
$OH + CH(CH_3)_2OH \xrightarrow{>90\%}$	2×10^9	15
$(CH_3)_2\dot{C}OH + H_2O$		
$H + CH(CH_3)_2OH$		16
$\nearrow (CH_3)_2\dot{C}OH + H_2$	1.8×10^8	
$\searrow \cdot CH_2CHOHCH_3 + H_2$	1.7×10^7	
$OH + (CH_3)_3COH \rightarrow$	4.2×10^8	15
$\cdot CH_2(CH_3)_2COH + H_2O$		
$H + (CH_3)_3COH \rightarrow$	1.0×10^5	16
$\cdot CH_2(CH_3)_2COH$		
$2CH_2OH \xrightarrow{96\%} (CH_2OH)_2$	2.4×10^9	17
$\xrightarrow{4\%} CH_2O + CH_3OH$		
$2CH_3\dot{C}HOH \rightarrow$	2.3×10^9	17
$CH_3CHO + CH_3CH_2OH$		
$2(CH_3)_2\dot{C}OH \rightarrow$	1.4×10^9	17
$(CH_3)_2CO + (CH_3)_2CHOH$		
$2 \cdot CH_2C(CH_3)_2OH \rightarrow$	1.4×10^9	17
$(CH_2C(CH_3)_2OH)_2$		
$e_{aq}^- + {}^-OOCHC=CHCOO^- \xrightarrow{pH\ 13}$	7.5×10^9	14
${}^-OOCCH=CHCOO^{2-}$		
$H + {}^-OOCHC=CHCOO^- \rightarrow$	4×10^9	16
${}^-OOCCH_2\dot{C}HCOO^-$		
$OH + HOOCHC=CHCOOH \rightarrow$	1.3×10^9	15
${}^-OOCCH(OH)\dot{C}HCOO^-$		
$Cu^+ + $ fumaric acid $\rightleftarrows$	$K = 9.0 \times$	13
$[Cu(fumaric)]^+$	10^3 M^{-1}	
$OH + Br^- \rightarrow OHBr^- \xrightarrow{Br^-,H^+}$	$>10^9$	18
$Br_2^- + H_2O$		

When N_2O-saturated solutions containing $(1-5) \times 10^{-4}$ M $Cu^{II}L$ and 1 M *tert*-butyl alcohol at the pH range of 3.5–10, in the presence and absence of phosphate buffer, were irradiated, none of the reactions reported in the argon-saturated solutions were observed.

N_2O-saturated solutions containing 3×10^{-4} M $Cu^{II}L$ and 0.2 M NaBr at pH 3.5–5 in the presence and absence of 0.1 M *tert*-butyl alcohol were irradiated. (Under these conditions over 85% of e_{aq}^- and OH radicals are transformed into $\cdot Br_2^-$ radicals and the rest into $\cdot CH_2C(CH_3)_2OH$ radicals (Table II).) The formation of a transient product with an absorption band with λ_{max} 320 nm and ϵ_{max} 1200 M^{-1} cm^{-1} was observed. This transient has a half-life considerably longer than 1 min. The formation of this transient causes a decrease of the specific conductivity which increases with decreasing pH.

Argon-saturated solutions containing 1×10^{-3} M $Cu^{II}L$, 1 M *tert*-butyl alcohol, 1×10^{-3} M phosphate, and $(1-5) \times 10^{-5}$ M fumarate in the pH range 4–5 were irradiated. The reaction kinetics observed at 410 and 350 nm was identical with that observed in the absence of fumarate under the same conditions. However in the presence of fumarate a final stable absorption
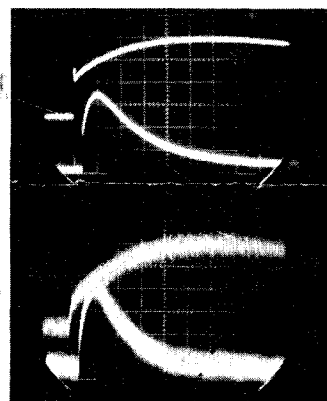

Figure 4. Oscillogram traces observed in solutions containing 2×10^{-4} M $Cu^{II}L$, 0.1 M ethanol, and 1×10^{-3} phosphate (pH 5.0, light signal 800 mV): (A) N_2O saturated [ordinate 10 mv/div and abscissa 500 μs/div (upper trace) and 5 ms/div (lower trace)]; (B) Ar saturated (ordinate 50 mv/div and abscissa as in A).

is observed at 350 nm (Figure 5).

N_2O-saturated solutions containing $(2-8) \times 10^{-4}$ M $Cu^{II}L$, 1×10^{-3} M phosphate, and 0.1 M methanol, ethanol, or 2-propanol in the pH range of 3.5–10 were irradiated. The formation of a transient with an absorption identical with that of the second transient in the *tert*-butyl alcohol–argon-saturated solutions was observed. The kinetics of decomposition of this transient, or stable product at pH >6.0, were also identical with those observed in the *tert*-butyl alcohol–argon-saturated solutions. However the yield of the transient was considerably smaller even when small pulse intensities were used. Thus $k(\cdot CH_2OH, CH_3\dot{C}HOH, (CH_3)_2\dot{C}OH + Cu^{II}L)$ $\leq 2 \times 10^6$ M^{-1} s^{-1} values were estimated though the reactions clearly occur (Figure 4).

When similar solutions were saturated with argon, results identical with those observed in the *tert*-butyl alcohol solutions were observed (Figures 1 and 4).

When neutral N_2O-saturated solutions containing 1×10^{-4} M $Cu^{II}L$, 0.1 M HCO_2Na, and 1×10^{-3} M phosphate (6.0 $\leq$ pH $\leq$ 7.0) are irradiated, three consecutive reactions are observed. The first reaction causes the formation of an intermediate with a weak absorption band at $\lambda \sim 410$ nm. This process is identified as the reaction $CO_2^- + Cu^{II}L \rightarrow Cu^IL + CO_2$ for which $k = 2.3 \times 10^9$ M^{-1} s^{-1} was reported.[1] This reaction is followed by a reaction causing a decrease in absorption at 410 nm and an increase in absorption at 320 nm. The rate of this reaction is identical with that of the first reaction observed in Ar-saturated solutions containing $Cu^{II}L$ + *tert*-butyl alcohol. This reaction is followed by a reaction which causes a decrease in absorption at 320 nm and a large increase in absorption at 410 nm, and the rate of this reaction is 7×10^2 s^{-1} again, identical with that observed in the *tert*-butyl alcohol system, the product of this reaction is stable in this pH range, at least for several minutes, and its absorption is slightly more than double that observed in the *tert*-butyl alcohol system.

Discussion

The radiolysis of water may be summed up by eq 1. The

$$H_2O \xrightarrow{\gamma,e^-} e_{aq}^-, OH, H, H_2, H_2O_2, H_3O^+ \qquad (1)$$
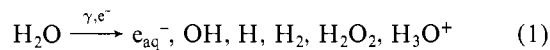
yields of these products are $G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$, and $G_{H_2O_2} = 0.75$ (where G is defined as the number of product molecules formed per 100 eV absorbed by the solution, 1 rd = 6.24×10^{13} eV g^{-1}).[7] Thus, by addition

(7) Matheson, M.; Dorfman, L. M. "Pulse Radiolysis"; M.I.T. Press: Cambridge, Mass., 1969.

of appropriate solutes to N_2O-saturated solutions containing $(1-5) \times 10^{-4}$ M $Cu^{II}L$, all the primary radicals e_{aq}^-, H, and OH are transformed into one aliphatic radical, $\cdot RH$ (Table II), with a yield of $G(\cdot RH) = 5.9$. (In solutions containing high concentrations of solutes, the radical yield is often somewhat larger, whereas the yields of H_2 and H_2O_2 are somewhat smaller.[7]) In argon-saturated solutions under the same conditions (Table II), $G(\cdot RH) = G_{OH} + G_H = 3.25$ and $G_{e_{aq}^-} = 2.65$.

The stable product formed in argon-saturated solutions containing $(1-10) \times 10^{-4}$ M $Cu^{II}L$ and 1 M alcohol at pH >7 is identified as Cu^IL. This identification is based on the identity of the absorption spectrum of this product with that of Cu^IL obtained electrochemically[3b] and is in full agreement with the conclusion of Tait et al.[1] and Papaconstantinou et al.[9] Furthermore, our conductometric results show that the formation of this product is accompanied by an increase in the conductivity as expected for the sequence of reactions 1 and 2. The observation that no transients which absorb at

$$e_{aq}^- + Cu^{II}L \rightarrow Cu^IL \qquad (2)$$
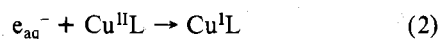
$\lambda > 320$ nm are formed in N_2O-saturated solutions containing $(1-5) \times 10^{-4}$ M $Cu^{II}L$ and 1 M *tert*-butyl alcohol indicates that the radical $\cdot CH_2C(CH_3)_2OH$ does not reduce $Cu^{II}L$ under our experimental conditions.

The spectra of the intermediates observed in argon-saturated solutions containing 3×10^{-4} M $Cu^{II}L$, 0.1 M *tert*-butyl alcohol, and 1×10^{-3} M phosphate at pH = 6.0 (Figure 1) differ considerably from those reported by Tait et al. for solutions at pH 7.0.[1] (However, no spectral changes in the pH range 6–7 are expected during the first 10 ms after the pulse (ref 1, Figure 4).) The main difference is that our results indicate that the spectra of the different intermediates consecutively formed differ not only in the absolute absorbance coefficients but also in shape. Thus our results clearly indicate that these intermediates differ chemically. This conclusion is further corroborated by the observation that the reactions observed cause large changes in the specific conductivity of the products.

The first intermediate observed in these solutions is identified as Cu^IL, formed in reaction 2. The following process is attributed to the reactions

$$Cu^IL + H_2O \rightarrow Cu^{III}L-H + OH^-$$
$$OH^- + H_3O^+ \rightarrow H_2O \qquad Cu^IL + H^+ \rightarrow Cu^{III}L-H \qquad (3)$$
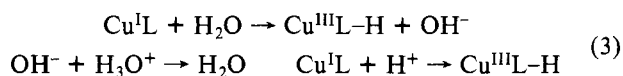
due to the following arguments:

(a) The conductivity measurements indicate that this process causes a decrease in the specific conductivity to its value prior to the pulse; i.e., the process consumes 1 equiv of H_3O^+.

(b) The reaction cannot be a reaction between Cu^IL and $\cdot CH_2C(CH_3)_2OH$ radicals, as the same reaction was observed in N_2O-saturated solutions containing HCO_2Na. In the latter solutions all the primary free radicals formed are transformed into CO_2^- (Table II), which reduce $Cu^{II}L$ to Cu^IL prior to this process.
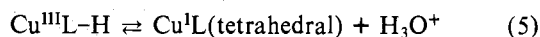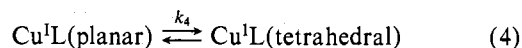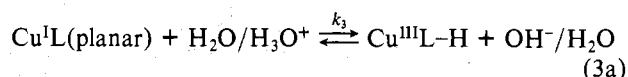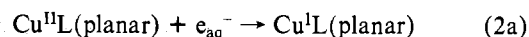
The absorption band of $Cu^{III}L-H$ differs considerably from that of Cu^IL (Figure 1) and has its maximum in the UV range, and we could only observe the tail of this absorption band starting at 350 nm.

The following reaction which is purely first order and causes an increase in the specific conductivity (Figure 3) has as its product a compound with an absorption spectrum identical with that of Cu^IL formed by electrochemical techniques.[3b,8] The increase in the specific conductivity is also in agreement with the idea that this reaction is the reverse process of reaction

3. However, this clearly cannot be correct:

(a) If reaction 3 is an equilibrium process, it cannot pass the equilibrium concentration.

(b) The absorption spectrum of the third intermediate, formed in this reaction, differs considerably from that of the first intermediate (Figure 1). We are thus faced with the conclusion that the third intermediate, which is a stable product at pH ≥ 6.0, is a form of Cu^IL different from that formed in reaction 2. The product of reaction 2 is most probably a planar form of Cu^IL as $Cu^{II}L$ is planar. On the other hand it is well-known that the preferred coordination of $Cu(I)$ is tetrahedral. We suggest therefore that the third intermediate is Cu^IL with a tetrahedral or distorted tetrahedral configuration. This suggestion is supported by the observation that Cu^IL does not coordinate carbon monoxide as a fifth ligand though analogous planar monovalent copper complexes do.[10] We suggest therefore that our observations are in agreement with the reaction sequence (2a)–(5). The ex-

$$Cu^{II}L(planar) + e_{aq}^- \rightarrow Cu^IL(planar) \qquad (2a)$$

$$Cu^IL(planar) + H_2O/H_3O^+ \underset{}{\overset{k_3}{\rightleftharpoons}} Cu^{III}L-H + OH^-/H_2O \qquad (3a)$$

$$Cu^IL(planar) \overset{k_4}{\rightleftharpoons} Cu^IL(tetrahedral) \qquad (4)$$

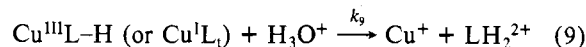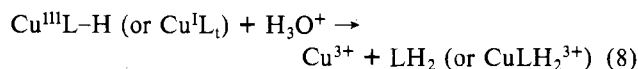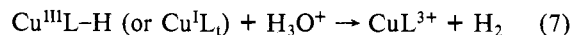$$Cu^{III}L-H \rightleftharpoons Cu^IL(tetrahedral) + H_3O^+ \qquad (5)$$

perimental data available is insufficient to decide whether reaction 4 or 5 occurs or possibly both reactions occur. The measured increase of the specific conducitivity of 160 $cm^2 \; \Omega^{-1}$ mol^{-1} at pH 5.0 caused by this reaction is only about 60% of that expected for the release of an equivalent of protons. Thus the results indicate that at this pH some $Cu^{III}L-H$ remains.

It is of interest to note that the product $Cu^IL_t \equiv Cu^IL$-(tetrahedral) is stable in N_2O-saturated solutions at pH ≥ 7.0 for at least 5 min. Thus the rate of reaction 6 has to be smaller

$$Cu^IL_t + N_2O \rightarrow Cu^{III}L + N_2 \qquad (6)$$
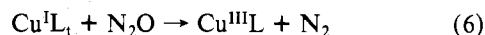
than 0.1 s^{-1}, though a rate of 1.7×10^6 M^{-1} s^{-1} was reported[1] for this reaction. The most plausible explanation of this discrepancy is that the N_2O of ref 1 contained as an impurity an oxidizing agent.

In acidic solutions, pH <5.5, the product Cu^IL_t is unstable and decomposes in a first-order process, the rate of which increases with decreasing pH (Figure 2). This reaction causes a decrease in the specific conductivity relative to the conductivity prior to the pulse and to a value equivalent to the consumption of one H_3O^+ equivalent (Figure 3). This process could be attributed to one of the following reactions:

$$Cu^{III}L-H \; (or \; Cu^IL_t) + H_3O^+ \rightarrow CuL^{3+} + H_2 \qquad (7)$$

$$Cu^{III}L-H \; (or \; Cu^IL_t) + H_3O^+ \rightarrow$$
$$Cu^{3+} + LH_2 \; (or \; CuLH_2^{3+}) \qquad (8)$$

$$Cu^{III}L-H \; (or \; Cu^IL_t) + H_3O^+ \overset{k_9}{\longrightarrow} Cu^+ + LH_2^{2+} \qquad (9)$$

The observation that in N_2O-saturated solutions containing $Cu^{II}L + NaBr$ at pH 3.5–5 a long-lived intermediate is formed, identified as $Cu^{III}L$[11] formed in the reaction $Cu^{II}L + Br_2^- \rightarrow Cu^{III}L + 2Br^-$, indicates that CuL^{3+} and (or) $CuLH_3^{3+}$ are (is) not formed during the decomposition of $Cu^{III}L-H$ or Cu^IL_t. Also $Cu^{3+}(aq)$ absorbs at $\lambda > 320$ nm and has at pH >4.5 a longer lifetime than Cu^IL_t.[12] We have therefore to

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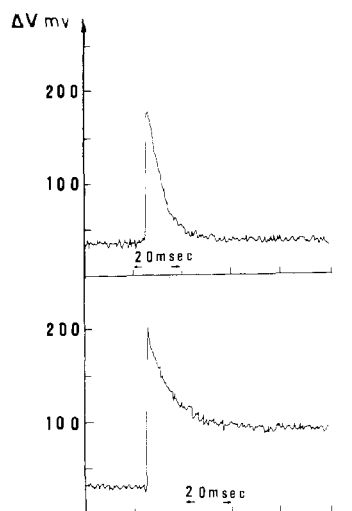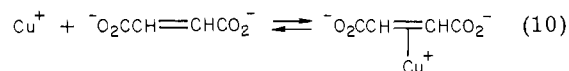(11) Meyerstein, D., unpublished results.

Figure 5. Computer output signal traces observed in Ar-saturated solutions containing 1×10^{-3} M $Cu^{II}L$, 1 M *tert*-butyl alcohol, and 1×10^{-3} M phosphate (pH 4.5): upper, total light signal 800 mV; lower, signal the same, but solutions contain, in addition, 5×10^{-5} M fumarate.

conclude that reaction 9 causes the decomposition of $Cu^{I}L_t$. Further support to this conclusion comes from the experiments in which Ar-saturated solutions containing 1×10^{-3} M $Cu^{II}L$, 1 M *tert*-butyl alcohol, 1×10^{-3} M phosphate, and $(2-5) \times 10^{-5}$ M fumarate at pH 4–5 were irradiated. Under these conditions all the primary radicals react with $Cu^{II}L$ and *tert*-butyl alcohol (Table II), and the fumarate is therefore not expected to affect the reaction kinetics. Indeed the rates of all the reactions observed were unaffected by the addition of fumarate. However, after the last reaction, a stable absorption at λ 350 nm remained (Figure 5.) The magnitude of this absorption was found to be proportional to the fumarate concentration. We attribute this absorption to the formation

of the d $\rightarrow \pi^*$ complex between Cu^+ and fumarate (eq 10).[13]

$$Cu^+ + {}^-O_2CCH{=\!=\!=}CHCO_2^- \rightleftharpoons {}^-O_2CCH{=\!\!\!\overset{\displaystyle |}{\underset{\displaystyle Cu^+}{=}}\!\!\!=}CHCO_2^- \quad (10)$$

Reaction 9 is acid catalyzed (Figure 2) in the pH range 4–5.5, and its rate is $(6 \pm 1) \times 10^6$ [H_3O^+] s^{-1}. At lower pH's, the pH dependence is considerably diminished. It is of interest to note that in the pH range 4–1 the rate increases from 350 to 2000 s^{-1}, i.e., has a value similar to that of reaction 4 or 5. It is thus tempting to speculate that these reactions are limited by the rate of conformational change of the ligand around the central copper cation.

The results (Figure 4) in the N_2O-saturated solutions containing methanol, ethanol, or 2-propanol indicate that the radicals $\cdot CH_2OH$, $CH_3\dot{C}HOH$, and $(CH_3)_2\dot{C}OH$ reduce $Cu^{II}L$, though the rates of these reactions are lower than 2×10^6 M^{-1} s^{-1}. All the following reactions are identical with those observed in the Ar-saturated *tert*-butyl alcohol solutions Table I. These results affirm the conclusion that the free radicals do not react with $Cu^{I}L$ under our experimental conditions.

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