Indeed, a very weak ferromagnetic coupling of -1.26 cm^{-1} was observed for $[Cu(L)(CH_3COO)_2]\cdot H_2O\cdot H_5OH$, which shows a similar geometry. Therefore, although the crystal structure suggests an alternating linear chain, it should be possible to interpret the data with a simple Bleaney–Bowers equation,[18] because the above considerations suggest that magneically the compound must behave as a chain of weakly interacting dimers. The curve calculated under this assumption fits satisfactorily the experimental points as shown in Figure 3, the systematic deviation of the curve at low temperature being probably due to the presence of a small amount of a paramagnetic impurity. The relative parameters are $g = 2.145$ (4) and $J = 431.7$ (6) cm^{-1} with the interaction Hamiltonian defined as $\mathcal{H} = J\mathbf{S}_1\mathbf{S}_2$. We attempted to fit the magnetic data in the hypothesis of an alternating chain, using the Duffy and Barr approach[19] in the development carried out by Hatfield et al.[20] The calculated values of the alternation parameter, α, were found very close to zero, as expected, and the fit did not improve significantly. Therefore, the magnetic data do not allow us to decide whether the description of the compound as an alternating chain is correct.

The EPR spectra recorded at room temperature show an asymmetric feature at $g = 2.08$ and no signal at half-field. This was checked by measuring the spectra at the maximum receiver gain setting of our instruments. The spectra do not change on lowering the temperature: they simply decrease in intensity but never show any hyperfine splitting.

The absence of any resolved hyperfine splitting, and of the $\Delta M = \pm 2$ transition, is indicative of a fast averaging of the triplet excitons; i.e., the spectra are a proof of the fact that the αJ value is much larger than either the fine or hyperfine splitting, whichever is the largest. Since in dimers bridged by oxamidate ligands D has been found[6] to be of the order of 0.01 cm^{-1}, even $\alpha J = 0.1$ cm^{-1} should be enough to yield exchange-narrowed spectra. Therefore, the EPR description of the magnetic properties of the present compound is that of an alternating chain. These results confirm that magnetic susceptibility and EPR spectra should be used together in order to take advantage of their complementarity.[21]

Registry No. 2, 100113-54-0; Cu(amoxa), 100113-55-1; $Cu_2(amoxa)(CH_3COO)_2$, 100113-57-3; diethyl oxalate, 95-92-1; neopentanediamine, 7328-91-8.

Supplementary Material Available: X-ray crystallographic data for $Cu_2(amoxa)(CH_3COO)_2$ including tables of anisotropic temperature factors for non-hydrogen atoms, positional parameters for hydrogen atoms, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Radiation Laboratory,
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Photochemistry of Copper(II)-Poly(acrylic acid) Complexes: Photogeneration and Photolysis of an Alkyl-Copper Intermediate

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The UV irradiation of complexes of copper(II) with carboxylic acids populate charge-transfer states that decay to an oxidized ligand and copper(I).[1-5] This behavior can be illustrated with $CuOCOCH_3^+$, which under 254-nm photolysis decomposes according to eq 1.[1,2] Recombination of the reactive products

$$CuOCOCH_3^+ \xrightarrow{h\nu} CT \longrightarrow [Cu^+,CH_3CO_2\cdot] \qquad (1)$$

following the rapid decarboxylation of the organic radical, eq 2–4,

$$[Cu^+,CH_3CO_2\cdot] \rightarrow CuOCOCH_3^+ \qquad (2)$$

$$[Cu^+,CH_3CO_2\cdot] \rightarrow [Cu^+,CH_3\cdot] + CO_2 \qquad (3)$$

$$[Cu^+,CH_3\cdot] \rightarrow CuCH_3^+ \qquad (4)$$

leads to metastable alkyl–copper intermediates, which exhibit strong optical absorptions in the near-UV, e.g. ca. 370 nm.[1-7]

The copper ion in the alkyl–copper intermediates can be regarded as ligated to the alkyl ligand by a covalent bond that favors an oxidation state much lower than 2+ for the metal. This suggests that some properties of the alkyl–copper species should approach those found in related copper(I) complexes, namely copper(I) hydrides, halides, and pseudohalides. Little is known, however, about the reactivity of the alkyl–copper intermediates under various conditions. In this regard, the investigation of the photochemistry of copper(II) ions complexes with polymeric carboxylic acids, e.g. poly(acrylic acids), serves the dual purpose of investigating the photochemistry of the polymeric complexes and the reactivity of alkyl–copper intermediates subject to interactions with a polyelectrolyte.

Experimental Section

Photochemical Procedures. Flash irradiations were carried out in an experimental setup described elsewhere.[8] For excitations, a Quanta Ray Nd Yag pumped dye laser was used as a source of 266-nm flashes with ca. 10 ns duration and ~20 mJ of energy. An average of at least 10 experiments, at each particlular wavelength, were used for the determination of transient spectra or the investigation of reaction kinetics. A fresh solution of photolyte, deaerated with streams of O_2-free nitrogen, was used for each irradiation. The ionic strength of these solutions was adjusted to 0.1 M with $NaClO_4$ and the acid concentration to pH 6.0 by titration with NaOH.

Titrations were followed with a combined reference–glass electrode and a high-impedance microvoltmeter. The complexation of copper(II) was established from determinations of Cu^{2+}(aq) ions with an electrode specific for copper ions and mathematical analyses of the equilibria reported for poly(acrylic acid)–copper(II) mixtures.[9] In the experiments reported below, the concentration of free copper(II) ions was less than 1% of the total copper(II) concentration, and the number of copper(II) ions per polyacrylic acid molecule was adjusted to values between one and eight.

Materials. Aldrich poly(acrylic acid) with an average formula weight of 5000, namely an average of 70 carboxylic groups per molecule, was purified by dialysis in a Spectra-Por dialysis tubing, fw cutoff 3000. The concentration of the resulting solution was estimated by titrating the acid with NaOH to neutral pH. Since the spectrum of polyacrylic acid in solutions with pH 6.0 exhibited an absorption band, $\lambda_{max} \sim 210$ nm, with an apparent extinction coefficient of 115 M^{-1} cm^{-1}, the optical density of the solutions was used for the verification of the acid concentration. Solutions of the copper–poly(acrylic acid) complexes were prepared by adding appropriate amounts of Analysis grade $Cu(ClO_4)_2$ to solutions containing a known concentration of poly(acrylic acid). Other materials were reagent grade and used without further purification.

Results

Flash photolysis of the Cu(II)–poly(acrylic acid) complexes produce transient spectra with maxima at 400 and 540 nm, Figure

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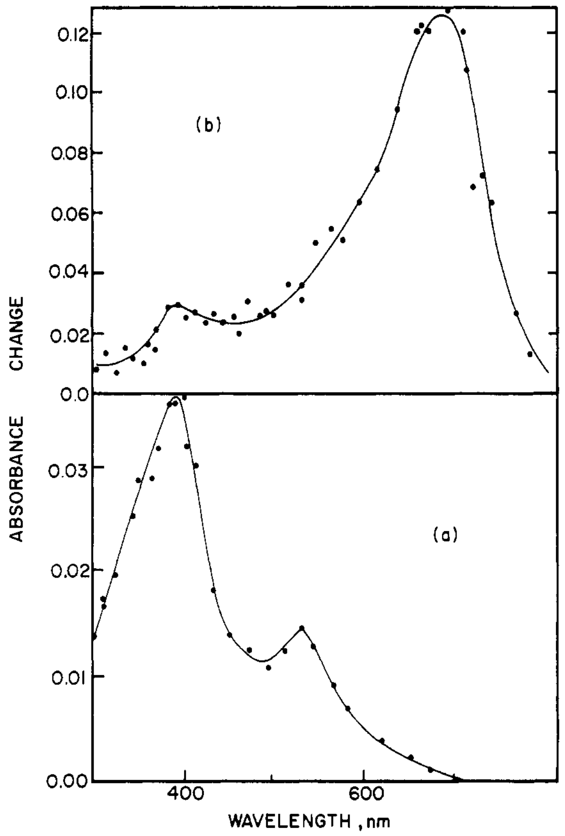

Figure 1. Transient spectra determined 30 ns after the 266-nm excitation of Cu(II)–poly(acrylic acid) complexes. The intensity of the flash required for the generation of curve a was nearly 1 order of magnitude smaller than that for the determination of curve b.

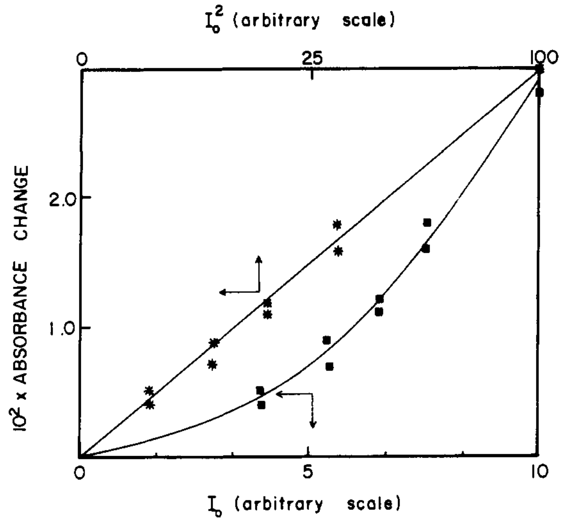

Figure 2. Dependence of the initial absorbance change at 650 nm (see Figure 1) on the flash intensity and the square of the flash intensity, respectively. The intensity scale is the normalized output of the photodiode used for probing the laser.[8]

1, which is typical of species produced in reactions between Cu(I) ions and alkyl radicals.[1-8] Although the features of these spectra are not very sensitive to the number of Cu(II) ions per polymer molecule[1-8] or the total copper(II) concentration in the experiment ($8 \times 10^{-5} \leq [Cu^{2+}] \leq 1.5 \times 10^{-3}$ M), it is dependent on the intensity of the flash. A new absorption band at 700 nm becomes more prominent than the 400-nm band as the intensity of the flash increases, Figure 1. Moreover the change in the optical density at 700 nm, determined after the flash, shows a second-order dependence on the intensity of the photolyzing pulse, Figure 2. The time resolution of the transient spectra shows that the band at 700 nm decays faster than the 400-nm band. Indeed, the band at 700 nm disappears within 500 ns by a process that is first order in transient concentration, $k = 8.8 \times 10^6$ s^{-1}, and regenerates some of the spectra produced with low-intensity flashes, Figure 3. The disappearance of the 700-nm band is accelerated in solutions saturated with N_2O. The faster rate of decay in N_2O-saturated solutions corresponds to a reaction rate constant, $k \sim 2 \times 10^8$ M^{-1} s^{-1}, for the reaction between N_2O and the transient.

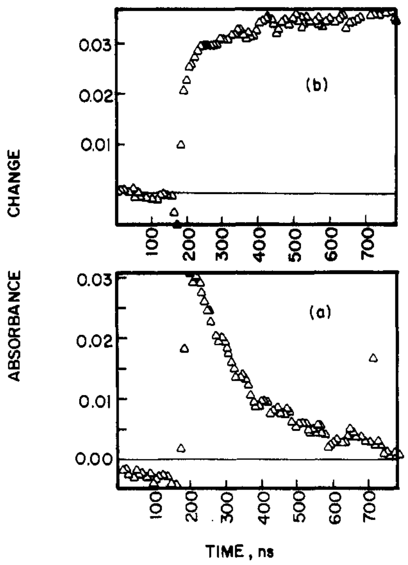

Figure 3. Traces for the rapid disappearance of the ~650 nm band (a) and the partial growth of the 400-nm band (b) at $t \geq 250$ ns for the spectrum shown in Figure 1b.

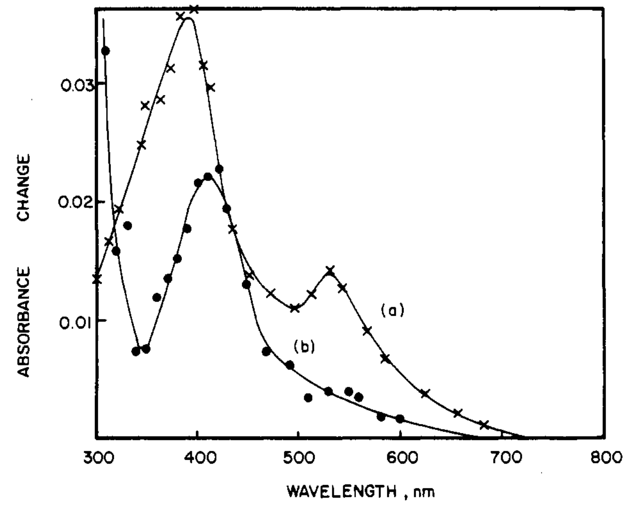

Figure 4. Transient spectra recorded at 30 ns (a) and 20 μs (b) for laser flash photolysis of Cu(II)–poly(acrylic acid) complexes with low-intensity flashes.

The rate of decay of the 540-nm band exhibits a first-order dependency on the concentration of the alkyl–copper transient and a more complex dependency on copper concentration. This process gives rise to spectral changes that signal the formation of a new intermediate, Figure 4.

Discussion

The photoreactivities of the Cu(II)–poly(acrylic acid) complexes and complexes with other monomeric carboxylic acids, e.g. acetate, are similar in that the primary process can be described as the photooxidation of the carboxylic group, eq 5.[10]

Decarboxylation of the radical derived from poly(acrylic acid), eq 6 and 7, is expected to be as fast a process as in the case of

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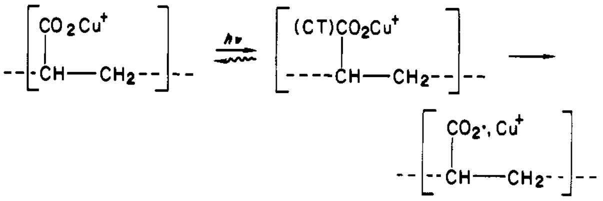
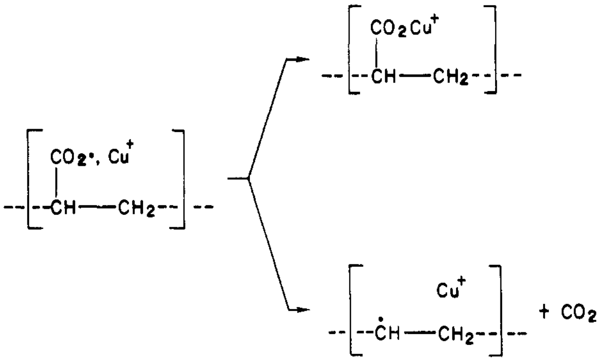
[10] Analyses of the 254-nm photolysis products, Cu(I) and CO_2, by procedures reported elsewhere,[2,3] reveal that for low intensities ($2 \times 10^{-4} \geq I_0 \geq 3 \times 10^{-5}$ einstein/(L min)) these products are formed in a 2:1 molar stoichiometry.

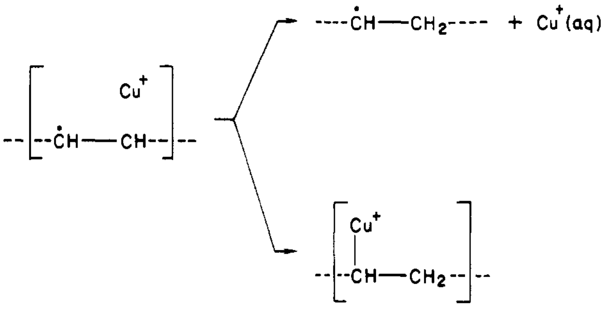

(5)

other related radicals.[11] On the basis of the reported spectra of alkyl–copper intermediates,[1–3,5,6] it is possible to assign the species produced with low-intensity flashes ($\lambda_{max} \sim 400$ nm, Figure 1) as an alkyl–copper complex, eq 7.


(6)

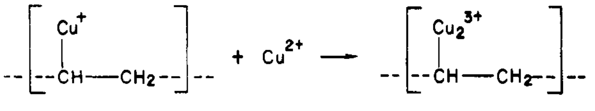
(7)

Moreover the short time that is required for the formation of such an alkyl–copper complex, $t < 50$ ns, suggests that it must be the product of geminate and secondary reactions of the decarboxylated radical and cuprous ions. The fact that spearation of the cuprous ions and methyl radicals from the bulk of the solution proved to be insignificant in the photodecomposition of $CuOCOCH_3^+$,[2] shows that a similar process, eq 8, under the attractive electrostatic potential of the poly(acrylic acid) must also lack relevance in photolysis of copper–poly(acrylic acid) complexes.

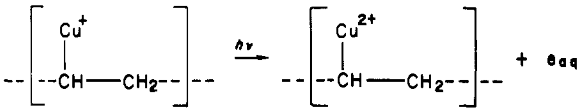

(8)

(9)

In this context, the spectral transformations observed in a 0.1–10 μs time domain, Figure 4, and the kinetics of such transformations, e.g. the dependence of the rate on free Cu(II) concentration, point to the formation of a dimeric alkyl complex when Cu(II) ions add to the monomeric alkyl–copper complex, eq 10.[12,13]

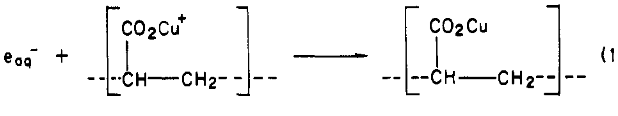

(10)

The spectrum and reactivity of the short lived species ($\lambda_{max} \sim 700$ nm, Figure 1) agree with those reported for the solvated electron.[14] The second-order dependence of the solvated electron concentration on light intensity, Figure 2, signals that such species is not a primary photochemical product and that it must be formed in a biphotonic process.[8] Such a biphotonic process can be associated with the secondary photolysis of the alkyl–copper intermediate, eq 11.[15]


(11)

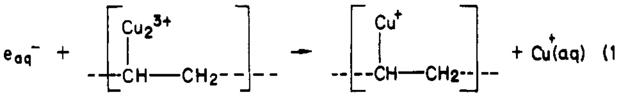
The fast decay of the solvated electron in our experiments must be related to various competitive reactions with scavengers that are present in solutions of the copper-polyacrylic acid complexes, eq 12–16. In this regard, the increase of the optical density at 400 nm during the decay of the electron in the absence of N_2O can be attributed to the regeneration of some of the primary alkyl–copper intermediate, eq 16. Since the formation of solvated electrons can be related to secondary photolysis of the monomeric alkyl–copper species and since Cu(I)–halide complexes have reactive CTTS states that decay in solvated electrons and Cu(II) species,[16,17] the photochemical properties of the monomeric alkyl–copper intermediate seem to be closer to those of the cuprous complexes than to those of the corresponding cupric compounds, a fact that signals a very high electronic density in the metal center.

$$e_{aq}^- + Cu^{2+}(aq) \longrightarrow Cu^+(aq) \qquad (12)$$


(13)

$$e_{aq}^- + H^+ \rightarrow H\cdot \qquad (14)$$

$$H^+ + e_{aq}^- + N_2O \longrightarrow N_2 + OH\cdot \qquad (15)$$


(16)

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Solid-State ^{13}C NMR Molecular Structure of Microcrystalline, Polymeric Me_2SnHPO_4

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Interest in the structure and bonding of organotin(IV) oxyphosphorus acid derivatives and in their possible use as commercial biocides has prompted the synthesis of a number of these compounds.[2–7] For the most part, they are high-melting, polymeric,

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