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Oxidation-Reduction Photochemistry. Intramolecular Electron Transfer in Cobalt(III)-Copper(I) Bridged Binuclear Ions

James K. Farr, Leslie G. Hulett, Robert H. Lane, and James K. Hurst*

Contribution from the Department of Chemistry, Oregon Graduate Center, Beaverton, Oregon 97005. Received October 3, 1974

Abstract: Photolytic oxidation-reduction reactions of $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{LCu}^{\text{I}}$ bridged binuclear ions, where L = alkenoic acids or primary aminoalkenes, are described. Excitation of $\text{Cu}(d) \rightarrow \text{L}(\pi^*)$ charge transfer bands causes intramolecular electron transfer between metal centers, $\Phi_{\text{Co(II)}} = 0.24-0.65$, according to the equation $(\text{NH}_3)_5\text{Co}^{\text{III}}\text{LCu}^{\text{I}} + 6\text{H}^+ \rightarrow \text{Co}(\text{II}) + \text{Cu}(\text{II}) + 5\text{NH}_4^+ + \text{HL}$. The first excited *singlet* charge transfer state is tentatively identified as photoreactive from studies on analogous intermolecular reactions. Results are rationalized in terms of electron transfer mediated by π -delocalized orbitals of the bridging ligands; for nonconjugated ligands, the pathway is provided by direct overlap of olefin π -antibonding orbitals with metal donor and acceptor orbitals. Irradiation in the wavelength region of the low-energy cobalt(III) ligand field bands (L_1) also causes photoredox decomposition in the binuclear ions, $\Phi_{\text{Co(II)}} \leq 1.3 \times 10^{-3}$.

Recent investigations of luminescence quenching of excited state organic¹ and inorganic² molecules, and of photosensitized redox decompositions,³ have led to the realization that electron transfer mechanisms can play a dominant role in these photochemical processes. In this report we present evidence for excited state electron transfer in bridged binuclear ions of the type RoLCu^{I} ($\text{Ro} \equiv (\text{NH}_3)_5\text{Co}^{\text{III}}$ moiety, $\text{L} = ^-\text{O}_2\text{C}(\text{CH}_2)_n\text{CH}=\text{CHR}$ or $\text{NH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$),⁴ arising from irradiation of either charge-transfer or metal-centered chromophores. Whereas photoredox decomposition of bridged binuclear ions has generally involved oxidation-reduction of ligands in addition to metal centers,^{5,6} reaction in the present systems comprises net electron transfer between metal centers.

Our interest in these reactions derives principally from our conviction that study of intramolecular redox processes⁷ offers the prospect of direct analysis for significant factors controlling the electron-transfer event, ambiguities associated with uncertainties in stabilities and structures of interacting partners inherent in intermolecular redox reactions being minimized. Electron transfer in the cobalt(III)-copper(I) binuclear ions at thermal energies is extremely slow

(generally, $t_{1/2} \geq 5$ years) despite a favorable reaction free energy;⁴ we have therefore examined their reactivity in electronically excited states. Comparison of rate data for various bridging ligands has provided evidence favoring electron transfer attending charge-transfer excitation which is mediated by olefin π -antibonding orbitals; the pathway is unique in that formal conjugation through the bridging ligand is not required.^{8,9} Limitations imposed by our studies upon mechanistic alternatives for photoredox reactions initiated by excitation in the cobalt(III) ligand field region are also discussed.

Experimental Section

Reagents. Carboxylatopentaamminecobalt(III) complexes were synthesized and characterized as previously described.⁴ The cobalt(III) complexes containing aminoalkene ligands were prepared by equilibrating dry dimethylformamide (DMF) solutions of Ro^-DMF perchlorate at ca. 60° for 1.5 hr with an excess of the amine; in these instances, the reaction was carried out under a blanket of nitrogen to minimize air oxidation of the organic ligand and molecular sieve (4A) was added to maintain anhydrous conditions. The complexes were isolated as their perchlorate salts after concentration on a rotary evaporator and recrystallized from hot dilute

aqueous perchloric acid. Visible spectra were characteristic of hexaammine complexes: for Ro-allylamine ion, $\lambda_{\max}(\epsilon_{\lambda}) = 478$ nm (67.4), 342 nm (57.5); for Ro-4-amino-1-butene ion, $\lambda_{\max}(\epsilon_{\lambda}) = 478$ nm (64.3), 341 nm (55.2). Elemental analyses were performed for Het-Chem-Co, Harrisonville, Missouri. Anal. Calcd for $((\text{NH}_3)_5\text{CoNH}_2\text{CH}_2\text{CH}=\text{CH}_2)(\text{ClO}_4)_3$: C, 7.21; H, 4.44; N, 16.82. Found: C, 7.23; H, 4.47; N, 15.63. Calcd for $((\text{NH}_3)_5\text{CoNH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2)(\text{ClO}_4)_3$: C, 9.35; H, 4.71; N, 16.37. Found: C, 9.56; H, 4.99; N, 16.48. Nmr chemical shifts and spin-spin splitting patterns for the vinyl protons were nearly identical for the primary amines (in CDCl_3) and their corresponding Ro complexes (in D_2O), although the RoL spectra were anomalous in that in neither case could transitions due to the methylene protons on the carbon atoms adjacent to the ammine nitrogen be detected. These resonances might well be broadened by spin coupling to the nitrogen protons in the cobalt complexes, coordination effectively blocking the rapid proton exchange occurring in free amines, and further obscured by overlapping transitions due to cis- and trans-coordinated NH_3 groups. Peaks ascribable to the β -methylene protons were observed to be superimposed upon the *trans*- NH_3 band in the Ro-aminobutene spectrum. Integrated intensities were consistent with the structures given. The ligand, 4-amino-1-butene, was prepared from the *N*-phthalimide derivative according to the procedures of Roberts and Mazur.¹⁰ Other chemicals were reagent grade and used without further purification.

Solutions of cobalt(III)-copper(I) binuclear ions were generally prepared in situ by reacting aqueous chromous perchlorate⁴ with deoxygenated solutions containing cupric and RoL perchlorate salts. Chromous ion reduction of nearly all of the RoL complexes was anticipated to be negligible under the experimental conditions relative to reduction of cupric ion (i.e., with $(\text{Cu(II)}) = 1.5 \times 10^{-2} M$, $(\text{RoL}) = 2.5 \times 10^{-3} M$, $(\text{H}^+) = 0.1 M$, $k_{\text{Cu(I)}} = 6.0 M^{-1} \text{sec}^{-1}$,¹¹ $k_{\text{Co(II)}} \leq 1.0 M^{-1} \text{sec}^{-1}$,¹² and therefore $(\text{Co(II)})/(\text{Cu(I)}) = k_{\text{Co(II)}}(\text{RoL})/k_{\text{Cu(I)}}(\text{Cu(II)}) \leq 0.03$; confirming this expectation, Co(II) ion could not be detected in reaction product solutions (analyzed for as the CoCl_4^{2-} ion).¹³ An exceptional case was the Ro-maleato ion, the chromous ion reduction of which is competitive with reaction by Cu(II) ion^{11,14} ($(\text{Co(II)})/(\text{Cu(I)}) = 6$). In this instance, cuprous ion was generated by reaction of chromous and cupric ions in the absence of Ro-maleato ion and subsequently mixed with the cobalt-containing solution after a time period sufficiently long to ensure complete reaction of the chromous ion.

Photochemical Methods. The illumination source for ultraviolet light was a Hanovia 200 W high-pressure mercury-xenon compact arc lamp mounted in a Bausch & Lomb mercury light source housing and powered by two Lambda Model LM E20 regulated power supplies. Emitted light was passed into a Bausch and Lomb high-intensity ultraviolet grating monochromator equipped with an achromatic condenser lens, then through the reaction cell. Incident light intensities controlled with variable width slits ranged over the values $I_0 = 0.04$ – 1.0×10^{-8} einstein sec^{-1} for various runs; intensities were routinely measured by ferrioxalate actinometry.¹⁵ Two ultraviolet filters (Corning CS 0-52) were used in the photosensitization experiments with 2,3-butanedione (biacetyl) at 410 nm to remove higher order diffractions and any high energy stray light. Cylindrical optical cells with 2-cm pathlengths were generally used as photolysis cells. Solution transmittances were recorded before and after each run using a Cary 16 spectrophotometer. Extensive decomposition of reaction solutions was required for the determination of ligand products by gas chromatographic methods (vide infra); reaction volumes in these instances were increased to ca. 240 ml to permit product accumulation (ca. 0.1 mmol) at reagent concentrations equal to those used in other studies. For these experiments, a photolysis cell was constructed from a 300-ml round-bottom flask by attaching a glass tubing which extended ca. $\frac{3}{4}$ the distance to the flask bottom to admit nitrogen gas for deoxygenation of reagent solutions and by glueing a flat circular quartz window over a hole blown in the side to admit ultraviolet light. Solutions were stirred magnetically during photolysis. To minimize ligand aqution during the relatively lengthy irradiation period required in these studies (2–10 hr) the cell was cooled to ca. 0° by partial immersion in a salt-ice bath. All other runs reported were made at ambient temperature.

Irradiations with visible light were performed using monochromatic light from either Coherent Radiation Model 52 continuous

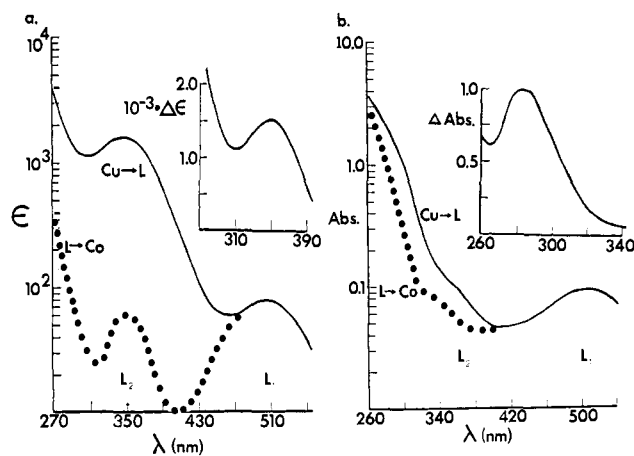


Figure 1. Spectra of Ro-carboxylate ions. (a) Dotted line, Ro-fumarato ion; solid line, Ro-fumarato-Cu(I) binuclear ion. (b) Dotted line, Ro-vinylacetato ion, $(\text{RoL}) = 5 \times 10^{-4} M$, $(\text{HClO}_4) = 0.1 M$; solid line, same conditions except $(\text{Cu(I)}) = 5 \times 10^{-4} M$. Difference spectra showing $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ bands are given in the insets.

wave argon ion or Model CR-MG mixed argon-krypton ion lasers. Cylindrical optical cells with 2-cm pathlengths were used as reaction vessels, the laser beam being defocused to provide approximately uniform light intensities across the surface of the cell windows. Incident light intensities, determined by Reineckate actinometry¹⁶ at the end of each run, were typically 0.2 – 1.5×10^{-6} einstein sec^{-1} . Solution transmittances were measured on a Cary Model 16 spectrophotometer immediately before and after each irradiation.

Biacetyl emission spectra were measured in 1 cm^2 optical cells using an Aminco-Bowman spectrophotofluorometer; solutions were excited at 410 nm with light from a xenon lamp source.

Quantum Yield Calculations. The extent of photoredox decomposition accompanying irradiation of ultraviolet charge transfer bands in the complexes was determined variously from absorbancy changes at the cobalt(III) L_1 ligand field band maxima or, for the binuclear ions, at the $\text{Cu} \rightarrow \text{L}$ charge transfer band maxima, or from direct spectrophotometric determination of Co(II) as the CoCl_4^{2-} ion.^{13,17} Consumption of Cu(I) and production of Co(II) generally occur with 1:1 stoichiometry,⁴ and photoaquation of RoL ions is apparently insignificant relative to photoredox decomposition (as judged by the identical results for cobalt reaction when determined by changes in the ligand field spectral bands or as CoCl_4^{2-}).⁴ Quantum yield calculations based on any of the analyses were therefore equivalent. Irradiation times were adjusted so that not more than 10% photochemical reaction had occurred.

Quantum yields were generally calculated from the equation

$$\Phi = \text{mmols reacted} / (I_a t \bar{f}) \quad (1)$$

where $I_a = I_0(1 - 10^{-\epsilon c l})$ is the average number of einsteins absorbed in unit time, t is the reaction time, and $\bar{f} = \overline{\text{Abs}}_{\text{Cu} \rightarrow \text{L}} / \overline{\text{Abs}}_{\text{total}}$ is the total average fraction of exciting light absorbed by the electronic state which leads to net photoreaction, here designated as the $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ transition. (Justification for the assignment is given in the Discussion section.) With fumarate, maleate, and cinnamate bridging ligands, the $\text{Cu} \rightarrow \text{L}$ band in the binuclear ions is strongly overlapped by the cobalt L_2 ligand-field transition⁴ (Figure 1); with allylacetate and vinylacetate linked ions extensive overlap with carboxylate ligand-to-cobalt charge-transfer (LMCT) bands occurs (Figure 1). The magnitude of \bar{f} therefore deviates markedly from unity in two instances: in the former systems when the total RoL ion concentration is in large excess (maximally, $(\text{RoL}) = 2.5 \times 10^{-3} M$, $(\text{Cu(I)}) = 2.5 \times 10^{-4} M$), absorption into the d-d band becomes extensive, with \bar{f} approaching 0.5; with the latter ions, fractional absorbancies as small as $\bar{f} = 0.15$ occur. An additional complication present with the allylacetate and vinylacetate bridged ions is that LMCT excitation causes extensive photoredox decomposition of the RoL ion, forming Co(II).^{5,18} Calculations of apparent quantum yields (Φ_{app}) from eq 1 using the total amount of cobalt reacted were corrected for direct photolysis of RoL by means of the equation

$$\Phi_{\text{corr}} = \Phi_{\text{app}} - \Phi_{\text{L} \rightarrow \text{Co}}(1 - \bar{f})/\bar{f} \quad (2)$$

where $\Phi_{\text{L} \rightarrow \text{Co}}$ is the quantum yield for photoredox decomposition arising from the excitation of the LMCT band and other terms are as previously described. For each photolysis run to which the correction was applied $\Phi_{\text{L} \rightarrow \text{Co}}$ values were determined independently by irradiation of solutions not containing Cu(I) but otherwise identical to those of the cobalt(III)-copper(I) ions. Potential effects of Cu(II) and Cr(III) ions present in the reactant solutions upon the competing photolytic decay processes were thereby taken into account.

Photoredox decomposition resulting from excitation with visible light was determined quantitatively by analysis for Co(II) as CoCl_4^{2-} .^{13,17} As Co(II) formation occurred only in solutions containing the binuclear ions, apparent quantum yields (Φ_{app}) calculated from eq 1 were corrected for absorption by RoL ions not coordinated to Cu(I); i.e.

$$\Phi_{\text{L}_1} = \Phi_{\text{app}}/\bar{f}_{\text{B}} \quad (3)$$

Since copper(I) coordination does not noticeably perturb the intensity of this transition, the average fractional quanta of light absorbed by the binuclear ions, $\bar{f}_{\text{B}} = \text{Abs}_{\text{RoLCu}}/\text{Abs}_{\text{RoLtotal}}$, was identical to the fractional molar concentration of binuclear ions, $(\text{RoLCu})/(\text{RoL})_{\text{total}}$; \bar{f}_{B} was therefore determined by calculation of the binuclear ion concentration for given reaction conditions using reported formation constants,⁴ when available, or estimated values upon constants reported for similar systems.¹⁹ Cu(I) was almost completely coordinated as the binuclear ion in any case under the reaction conditions. The errors introduced by these approximations were therefore small.

Ligand Analysis. Carboxylate ligands labilized during photolysis were recovered by ether extraction of the irradiated solutions. For these investigations photolysis was allowed to proceed until ca. 25% complex had reacted. Stepwise procedures were: (a) removal of metal ions by cation exchange chromatography (Bio-Rad AG-50W-X8, H^+ -form) (in this, the chromatography column was thermostated at 0° to minimize aequation of the adsorbed RoL ions); (b) concentration of the eluent by vacuum distillation on a rotary evaporator; (c) reduction of the solution acidity to pH ~2 with KOH to minimize uptake of mineral acids in the ether phase; (d) filtration at 0° to remove precipitated KClO_4 ; (e) extraction with ether using a continuous liquid-liquid extraction apparatus. Nonvolatile ligands (fumarate, maleate, cinnamate) were recovered as solid residues by distillation of the ether phase and identified by proton nmr (Varian HA-100, in $\text{DMSO}-d_6$) and absorption infrared (Perkin-Elmer Model 621, KBr pellet) analyses. Quantitative determinations of the free organic ligands were made from ultraviolet absorption spectra of aliquots of the aqueous solutions after chromatographic removal of the metal cations. Spectral parameters taken for these analyses were: fumarate, $\epsilon_{205} = 1.57 \times 10^4$ (pH 4.6); maleate, $\epsilon_{208} = 1.46 \times 10^4$ (pH 4.6); cinnamate, $\epsilon_{278} = 2.3 \times 10^4$ (pH 1.0); acrylate, $\epsilon_{240} = 112$.

The nonconjugated ligands, allylacetate, vinylacetate, and allylamine, gave no suitable chromophores for spectral analysis. Etheral solutions of the isolated carboxylic acids were methylated with diazomethane, concentrated by fractional distillation, and analyzed by quantitative gas chromatography (Varian Aerograph, Model 1700, Carbowax column, flame ionization detection), concentrations of methyl esters being determined by comparison of peak areas with standard solutions of authentic samples of the alkanoate methyl esters.

Allylamine reacted extensively with the cation exchange resin, precluding its use in isolation of the free amine. Gas chromatographic analysis could not be undertaken in the presence of RoL as it was found that large amounts of the coordinated amine were labilized under the reaction conditions. The procedure adopted involved concentration of the irradiated solutions by rotary evaporation, addition of KOH to strongly alkaline conditions, centrifugation to remove precipitated metal hydroxides and KClO_4 , and manual extraction several times with chloroform. All steps beyond the addition of KOH were done as rapidly as possible with solution temperatures maintained near 0° to minimize base-catalyzed hydrolysis of the ligands. The chloroform solutions were analyzed quantitatively by gas chromatography (Varian Aerograph, Model 1700, polystyrene column, flame ionization detection), peak areas

being compared to reference standard solutions of allylamine in CHCl_3 .

Results

Quantum Yields. (a) Irradiations in the $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ Charge Transfer Spectral Regions. Quantum yields for photodecomposition resulting from irradiations of the cobalt(III)-copper(I) ions at or near the $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ spectral maxima⁴ are recorded in Table I. Values for all entries except allylacetate and vinylacetate ligands were obtained from eq 1; for the latter ions eq 2 was used to correct for the substantial (16-76% total Co(II) formed) photodecomposition accruing from direct irradiation of the carboxylate-to-cobalt (LMCT) charge-transfer transitions. Quantum yields were independent of reactant ion concentrations over the ranges $(\text{HClO}_4) = 0.1-1.0 \text{ M}$, $(\text{RoL})_{\text{total}} = 2.5-25 \times 10^{-4} \text{ M}$, $(\text{Cu(I)})_{\text{total}} = 2.5-10 \times 10^{-4} \text{ M}$, with $(\text{RoL})/(\text{Cu(I)}) = 1.0-10$, and independent of absorbed radiation fluxes varied from $I_m = 0.6-8 \times 10^{-5} \text{ einstein l}^{-1} \text{ min}^{-1}$. They were also independent within the error limits cited in Table I of energies of exciting light varied over the width of the $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ band (Figure 2).

Photoredox quantum yields arising from LMCT excitations of the RoL ions were determined from spectral changes in the cobalt ligand field bands. Average values obtained were: for Ro-vinylacetate ion, $\Phi_{\text{Co(II)}} = 0.39 \pm 0.06$, irradiated at 280-290 nm; for Ro-allylacetate ion, $\Phi_{\text{Co(II)}} = 0.33 \pm 0.04$, irradiated at 290 nm; for Ro-acrylate ion; $\Phi_{\text{Co(II)}} \approx 0.16$ irradiated at 310 nm. Reaction solutions contained in addition to the RoL ions $(\text{Cu(II)}) = 1.5 \times 10^{-2} \text{ M}$, $(\text{Cr(II)}) = 2.5-10 \times 10^{-4} \text{ M}$, pH 0-1 (HClO_4). Quantum yields obtained for individual runs were used in calculations involving eq 2. Reactions of all other RoL ions at the irradiation wavelengths used in this study were negligible in the absence of Cu(I) ion.

Implicit in the calculations is the assumption that $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ excitation is the primary photochemical event leading to net reaction; for systems containing strongly overlapping bands (cf. Figure 1) the alternative possibility exists that the other excited states lie on the reaction pathway. Quantum yields were therefore calculated from eq 1 and 2 assuming that enhanced photoreactivity in the cobalt L_2 ligand field or LMCT charge-transfer bands occurs with Cu(I) coordination and that the $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$ excitation is deactivated by photophysical processes not leading to redox decomposition. Quantum yields calculated in this fashion were found to vary widely, generally increasing with decreasing reagent concentrations over the range $\Phi_{\text{Co(II)}} = 0.1-2.8$ and increasing with decreasing excitation energies (Figure 2).

No oxidation-reduction could be detected within 24 hr in solutions protected from light which contained Cu(I) and the Ro-amine ligands. As with the Ro-carboxylate-Cu(I) ions,⁴ electron transfer by thermal pathways is extremely slow in these binuclear ions.

Copper-to-ligand charge-transfer excitation of Cu(I) π -complex ions of the alkenoates and aminoalkenes which serve as bridging ligands in the cobalt(III)-copper(I) ions generally resulted in only minor photodecomposition; quantum yields based upon the small spectral losses accompanying extensive uv irradiation were estimated at $\Phi \leq 10^{-2}$. An exception was the Cu(I)-maleate ion, for which irradiation at 340 nm caused a bathochromic shift in the position of the $\text{Cu} \rightarrow \text{L}$ band maximum, suggestive of isomerization to the *trans*-fumarate ion. Confirmation of this effect was gained by proton NMR analysis of ligands isolated from irradiated solutions. The yield of recovered acid was 82-92%, with up to 20% present as fumarate. No fumaric acid was found in ligand recovered from identical solutions which

Table I. Quantum Yields for Ro-L-Cu Ion Photodecomposition^a

L	Irradiation wavelength, nm	Φ^b	Irradiation wavelength, nm	$10^4\Phi^c$
$\text{O}_2\text{CCH}=\text{CH}_2$	320	0.24 ± 0.04 (9)	514.5	1.0 ± 0.1
$\text{O}_2\text{CCH}=\text{CHCOOH}$ (trans)	350	0.33 ± 0.07 (17)	514.5	5.9 ± 1.1
$\text{O}_2\text{CCH}=\text{CHCOOH}$ (cis)	343	0.37 ± 0.05 (5)	514.5	6.5 ± 0.4
$\text{O}_2\text{CCH}=\text{CHC}_6\text{H}_5$	340	0.31 ± 0.04 (4)	514.5	7.3 ± 0.3
$\text{O}_2\text{CCH}_2\text{CH}=\text{CH}_2$	290	0.65 ± 0.14 (8)	514.5	12 ± 2
$\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	290	0.42 ± 0.09 (3)	514.5	8.0 ± 0.9
$\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$	300	0.65 ± 0.06 (4)	488.0	0.7 ± 0.1
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	290	0.57 ± 0.09 (8)	488.0	≈ 0.1

^a Experimental conditions given in text. ^b Number of individual runs given in parentheses; error limits are average deviations from mean values. ^c Average of duplicate determinations; error limits give the range of values obtained.

Table II. Ligand Recovery from Ro-L-Cu^I Near-Uv Irradiations^a

Ligand (L)	Ro reacted, mmol	Ligand recovered, ^b mmol	(L)/(Ro)	Methods
$\text{O}_2\text{CCH}=\text{CH}_2$	0.0031	0.0032	1.0	Uv
$\text{O}_2\text{CCH}=\text{CHCOOH}$ (trans)	0.16, 0.15	0.16, 0.14	1.0, 0.93	Uv, NMR, ir
$\text{O}_2\text{CCH}=\text{CHCOOH}$ (cis)	0.13, 0.049	0.14, 0.055	1.1, 1.1	Uv, NMR, ir
$\text{O}_2\text{CCH}=\text{CHC}_6\text{H}_5$	0.024, 0.017	0.021, 0.016	0.88, 0.95	Uv, NMR
$\text{O}_2\text{CCH}_2\text{CH}=\text{CH}_2$	0.10	0.091	0.91	GC
$\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	0.027	0.024	0.89	GC
$\text{NH}_2\text{CH}_2\text{CH}=\text{CH}_2$	0.21	0.16	0.76	GC

^a Experimental conditions given in text. ^b Corrected for manipulative losses and ligand labilization resulting from reactions other than Cu → L band irradiations; magnitudes of error limits vary with analytical methods but are typically ca. 10%.

were not irradiated, nor were proton peaks ascribable to other species present in the NMR spectra. Quantum yields estimated for the isomerization are high, $\Phi_{\text{cis} \rightarrow \text{trans}} = 0.4-0.8$.

(b) **Irradiations of Cobalt L₁ Ligand Field Bands.** Quantum yields for Co(II) formation from binuclear ions irradiated with visible light (carboxylato bridging ligands, λ irradiation = 514 nm; ammine bridges, $\lambda_{\text{irrad}} = 488$ nm) are given in Table I. The corresponding absorption maxima for the low-energy ligand field transitions in the Ro-carboxylato and Ro-ammine ions are 503 and 478 nm, respectively. For all runs (RoL)_{total} = 2.5×10^{-3} M, (Cu(I))_{total} = (Cr(III)) = 2.0×10^{-3} M, Cu(II) = 1.3×10^{-2} M, pH 1.0 (HClO₄). Cobaltous ion could not be detected in irradiated solutions which did not contain Cu(I), but were otherwise identical to the binuclear ion solutions. Based upon the irradiation times and sensitivity limits of the analytical methods, an upper limit of $\Phi_{\text{Co(II)}} \leq 10^{-5}$ can be set for the Cu(I)-free solutions.

The photochemical redox behavior of Ro-vinylacetato-Cu(I) ion was examined over a wider range of experimental conditions. Quantum yields were independent within experimental error of reactant ion concentrations over a sixfold range in variation, (RoL)_{total} = $1.2-7.6 \times 10^{-3}$ M, (Cu(I))_{total} = $1.0-6.0 \times 10^{-3}$ M, with (RoL)/(Cu(I)) = 1.25, and of absorbed radiation flux over a fivefold range, $I_m = 1.6-9 \times 10^{-3}$ einstein l⁻¹ min⁻¹, irradiated at 514.5 nm. Measured quantum yields were unaltered by incorporation of a plasma filter into the optical train to remove stray light. Yields increased markedly with increasing excitation energy over the width of the L₁ band, however. In duplicate runs with the reagent concentrations given in the preceding paragraph, the following values were obtained: $\lambda(10^4\Phi_{\text{Co(II)}}) = 530.9$ nm (6.2 ± 0.2), 514.5 nm (11.6 ± 1.9), 488.0 nm (13.8 ± 0.5), 476.5 nm (17.5 ± 0.5), a threefold variation.

Photoaquation of RoL was apparent in all solutions from absorbancy losses in the ligand field bands. Products were not identified, but quantum yields of $\Phi_{\text{aquation}} = 10^{-4}-10^{-3}$ could be estimated. These very crude values compare favorably with photoaquation yields for other cobalt amines;^{5,20} Co(II) was found to be only a minor photoreaction product in these studies as well.

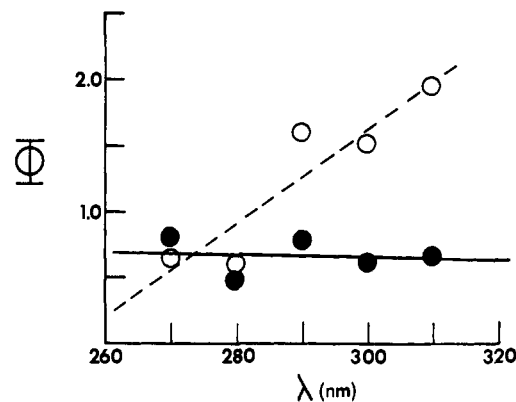


Figure 2. Wavelength dependence of quantum yields for photoredox decomposition of Ro-vinylacetato-Cu(I) ion. (RoL) = Cu(I) = $2.5-10 \times 10^{-4}$ M; (HClO₄) = 0.1 M. Solid circles, calculated assuming Cu(d) → L(π^*) excitation initiates reaction; open circles, assuming carboxylate-to-cobalt LMCT excitation is causative. Data points are averages of duplicate determinations; error limits are ca. $\pm 15\%$.

Stoichiometry of the Photochemical Reaction. Comparisons of the quantities of the bridging ligands labilized with the extent of photoreactions arising from ultraviolet irradiations of the cobalt(III)-copper(I) binuclear ions are given in Table II; close 1:1 correspondence is evident. For these reactions, (RoL)_{total} = $2-4 \times 10^{-3}$ M with (Cu(I))_{total} adjusted so that RoL was in slight excess, pH 1.0 (HClO₄). Reported values for ligand recovery are corrected for manipulative losses and for aquation occurring during photolysis and subsequent ligand isolation. Ligand losses during isolation were estimated from procedural treatment of reference solutions containing approximate concentrations of reactant solutions after irradiation; for uv spectral determination, the losses were negligible, for gas chromatographic analyses of carboxylate esters, losses were ca. 10%, and for recovery of the amine, losses were 20%. Aquation of Ro-carboxylato ions was likewise small, accounting for less than 5% of the total ligand released, but the amine recovered from the blank was 15% the total recovered, the relatively large amount presumably reflecting base-catalyzed hydrolysis occurring during ligand recovery. The entries for R-vinylace-

tato-Cu(I) and Ro-allylacetato-Cu(I) irradiation were also corrected for photodecomposition resulting from absorption by the carboxylate-to-cobalt charge-transfer bands; $(L)/(Ro) = 0.39$ was determined for Ro-vinylacetato ion by irradiation in the absence of Cu(I), decomposition by this pathway accounting for 15% of the total recovered ligand in photolysis of the binuclear ions; no carboxylate ligand could be recovered from irradiated solutions of the Ro-allylacetato ion.

Nonvolatile organic ligands recovered were unambiguously identified as the bridging ligands by comparison of their infrared and proton NMR spectra with authentic samples. No indication of formation of other organic compounds was found nor was there any evidence of cis-trans isomerization of labilized maleic or fumaric acids. Carboxylate methyl esters cochromatographed with reference samples of the bridging ligand methyl esters, as did recovered labilized ammine with allylamine.

No CO_2 or other gases which might be formed by ligand photooxidation¹⁸ could be detected in product solutions from Ro-fumarato-Cu(I) ion photolyses; mass spectrometric and gas chromatographic (10% nickel catalyst column) analyses were made.

Other Experiments. Photoinduction of intermolecular redox decomposition was attempted by irradiation of $Cu(d) \rightarrow L(\pi^*)$ bands of Cu(I) π complexes in the presence of potential RoL acceptor ions. For these experiments anaerobic solutions of Ro-acetato ion and copper(I) π coordinated to allyl alcohol were prepared, Cu(I) being generated in situ by reaction of chromous ion with excess copper(II). Competitive Cr(II) ion reduction of Ro-acetato ion was negligible under the experimental conditions (vide infra).^{11,21} With Cu(I) formation there appeared an intense absorption band at 290-300 nm, ascribable to the $Cu(d) \rightarrow L(\pi^*)$ transition of the Cu(I)-allyl alcohol π complex.⁴ Excitation of this band in the presence of Ro-acetato ion produced no detectable net photoreaction, quantum yields for cobalt(II) reduction being $\Phi_{Co(II)} \leq 10^{-2}$, based upon the experimental conditions and sensitivity of analytical methods. Two reaction solutions were irradiated: (a) (Ro-acetato) = $2.6 \times 10^{-3} M$, $(CH_2=CHCH_2OH) = 0.1 M$, $(Cu(I))_{total} = (Cr(III)) = 1.0 \times 10^{-2} M$, $Cu(II) = 10^{-2} M$, $(HClO_4) = 0.1 M$; (b) (Ro-acetato) = $1.0 \times 10^{-3} M$, $(CH_2=CHCH_2OH) = 2 \times 10^{-2} M$, $(Cu(I))_{total} = Cr(III) = 1.5 \times 10^{-3} M$, $(Cu(II)) = 1.5 \times 10^{-2} M$, $(HClO_4) = 0.1 M$.

The possibility of photosensitization of intramolecular electron transfer in the cobalt(III)-copper(I) ions by energy transfer from electronically excited donor molecules was also briefly investigated. Irradiation of the organic carbonyl donor, biacetyl, at the wavelength corresponding to excitation to its first singlet state (410 nm) in solutions containing acrylate, allylacetate, or allylamine bridged ions gave no indication of net reduction of cobalt(III), $\Phi_{Co(II)} \leq 10^{-3}$. For these experiments $(RoL)_{total} = 1.5 \times 10^{-3} M$, $(Cu(I))_{total} = (Cr(III)) = 1.0 \times 10^{-3} M$, $(Cu(II)) = 1.0 \times 10^{-2} M$, $(biacetyl) = 0.13 M$, $I_m = (1-7) \times 10^{-5}$ einstein $l^{-1} \text{ min}^{-1}$. Biacetyl phosphorescence at 515 nm was strongly quenched by $1.5 \times 10^{-3} M$ RoL ions (88-91%) and by $10^{-2} M$ Cu(II) (85%) and moderately quenched by $10^{-3} M$ Cr(III) (58%), although in no instance was biacetyl fluorescence at 460 nm markedly changed.

Discussion

Charge-Transfer Photochemistry. (a) Nature of the Photoredox Reactions. Quantum yields calculated in the present manner are diagnostic of the primary photoexcitation process(es) leading to chemical reactions. Thus, the assumptions that cobalt ligand field or charge-transfer excitations account exclusively for the enhanced reactivity of the

binuclear ions are untenable on several counts. First, although the observed wide variation in quantum yields calculated from these assumptions might conceivably be attributable to excited state quenching by reactant ions, no quantitative correlation with reagent concentrations could be found when several simple bimolecular mechanisms were tested. Second, the magnitudes of quantum yields suggest radical reaction mechanisms, but are generally insensitive to or increase with the concentration of free cuprous ion, which should act as an effective radical scavenger. Third, it is difficult to account by simple mechanisms for the apparent increases in $\Phi_{Co(II)}$ with decreasing excitation energy (Figure 2). Finally, the extensive photodecomposition observed with binuclear ions bridged with acrylate and the aminoalkene ligands cannot in any case be rationalized on the basis of initial population of cobalt excited states;²² here, energies required for ligand-to-cobalt charge-transfer excitation are substantially greater than that of the incident photons and overlap with the L_2 band is inappreciable.

On the other hand, quantum yield calculations based upon the assumption that $Cu(d) \rightarrow L(\pi^*)$ excitation leads to photoredox decomposition are totally consistent with simple photochemical mechanisms. Since direct excitation to the cobalt L_1 and L_2 ligand field excited states (the latter could be demonstrated for aminoalkene bridged ions only) does not give appreciable Co(II) formation, it is apparent that the charge-transfer excitation is the primary photochemical event leading to net oxidation-reduction. Furthermore, from the constancy of $\Phi_{Co(II)}$ values measured over widely varying reagent concentrations we infer that redox occurs principally by intramolecular electron transfer.

The near quantitative recovery of organic ligands, taken with the previously determined⁴ 1:1 stoichiometric one-electron cobalt(III) reduction and reaction of copper(I), is consistent with the equation: $6H^+ + Ro-L-Cu(II) \rightarrow Co(II) + Cu(II) + HL + 5NH_4^+$, oxidation-reduction occurring principally by net electron transfer between metal centers. The alternative of reduction of both metal ions with oxidation of coordinated amines appears remote, particularly in view of the fact that significant ammine oxidation has never been observed in the photoredox decompositions of RoL compounds.^{5,18} The excess RoL reduced over Cu(I) reacted as previously reported for Ro-vinylacetato-Cu(I) and Ro-allylacetato-Cu(I) ions⁴ is accounted for by redox decomposition resulting from direct irradiation of the ligand-to-cobalt charge-transfer bands.

(b) The Photoreactive State. Electron transfer might occur directly from the initially excited $Cu(d) \rightarrow L(\pi^*)$ singlet state or from any of several low-lying triplet states, i.e., cobalt ligand field, ligand-to-cobalt or copper-to-ligand charge transfer, arrived at by intersystem crossing and internal conversion processes. A basis for distinguishing between electron transfer from excited singlet or triplet states is provided by the studies on intermolecular redox decomposition with Ro-acetato and Cu(I)-allyl alcohol reactants. If intramolecular electron transfer occurs from the triplet state manifold, then necessarily both intersystem crossing and electron transfer probabilities must be high to account for the large quantum yields measured for electron transfer. Given the absence of apparent mixing of electronic states of the chromophores,²² population of cobalt(III) excited states by energy transfer from copper(I) probably occurs by processes equivalent to bimolecular quenching mechanisms.²³ Excitation to cobalt(III) triplet states by resonance transfer mechanisms is unlikely because transitions for the acceptor chromophores are spin forbidden; efficient intersystem crossing therefore requires collisional interactions (exchange energy transfer). Crossing efficiencies of the excited $Cu(d) \rightarrow L(\pi^*)$ singlet to accessible triplet states should be

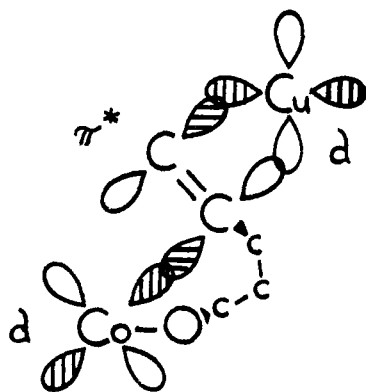
grossly approximate whether arising from nominally intramolecular or intermolecular interactions. Likewise the probability of collisional deactivation in excited triplet states leading to net electron transfer, if facile in the binuclear ion, should occur to a measurable extent in the Roacetato, Cu(I)-allyl alcohol model. However, no detectable intermolecular redox occurs, implying that either intersystem crossing or triplet electron transfer probabilities are not favorable. We tentatively conclude, therefore, that the Cu(d) \rightarrow L(π^*) singlet state is photoreactive in the binuclear ions.

Loss of biacetyl phosphorescence in the photosensitization experiments is consistent with efficient transfer of energy from the biacetyl triplet state to the triplet manifold of states of components of the reaction solutions, although alternative quenching mechanisms not involving electronic energy transfer cannot be excluded.^{3,5,24,25} Energies of potential acceptor charge-transfer triplet states are not accurately known, but may be comparable to that of the biacetyl donor triplet.²⁶ Given these reservations, the results are consistent with assignment of photoredox reactivity to the Cu(d) \rightarrow L(π^*) singlet state, i.e., no evidence of reaction from triplet states can be found.

(c) **Reaction Pathways.** Electron transfer through extended π -conjugated orbitals of bridging ligands has been proposed to account for the thermal oxidation-reduction behavior of certain transition metal ions^{8,9} and a theoretical basis for the phenomenon has been described.²⁸ Photoinduced electron transfer observed in the present systems containing π -conjugated bridging ligands (Table I, the first four entries) is consistent with this conceptual view; nonetheless, electron transfer remains facile with the introduction of methylene groups which effectively disrupt conjugation between the metal centers (Table I, the last four entries). The possibility of electron tunneling through the barrier imposed by methylene groups is precluded by the insensitivity of quantum yields to the lengths of the methylene chains.²⁹ Chelation by the carbonyl oxygen of cobalt-binding carboxyl groups in the reactive excited state molecules might provide an electron transfer pathway for the nonconjugated carboxylate ligands, but this rationalization is clearly untenable for the amine ligands which possess no low-energy orbitals suitable for formation of coordinate bonds to Cu(I).

For the nonconjugated binuclear ions, a pathway comprising electron transfer mediated by direct overlap of the olefin π^* orbitals with metal donor and acceptor orbitals is consistent with the data. (Scheme I: the amine ligands and

Scheme I



carbonyl oxygen and protons of allylacetate have been omitted.) Net electron transfer requires that the ligand assumes a folded conformation; model-building studies indicate that geometries are readily achieved which provide significant

overlap of the relatively diffuse olefin π^* orbitals with either π -symmetry or σ -symmetry cobalt-acceptor orbitals (in the latter case in a distorted octahedral environment). The radial redistribution of electron density accompanying population of the Cu(d) \rightarrow L(π^*) singlet state can reasonably be expected to initiate electron transfer by this pathway; electron transfer might proceed with formation of a discrete olefin radical-anion intermediate or by electron tunneling.²⁸

Other pathways which do not invoke mediation of electron transfer by appropriately oriented olefin groups might be written, e.g., formation of incipient ligand radical cations by charge transfer to cobalt(III) followed by scavenging of the ligand cation by Cu(I), but appear less likely on the basis of our assignment of the photoreactive state.

Ligand Field Photochemistry. Quantum yields for Co(II) formation decrease ca. 10^3 -fold when the binuclear ions are irradiated in the cobalt(III) ligand field spectral region; a marked dependence upon the identity of the bridging ligand is also apparent (Table I). Electron transfer is intramolecular, at least for Ro-vinylacetato-Cu(I) ion, as judged by the independence of $\Phi_{\text{Co(II)}}$ upon reactant ion concentrations. The possibility that reaction occurs by excitation to charge-transfer states arrived at by absorption of a second photon by cobalt(III) in a ligand field excited state can be dismissed from the observation that quantum yields are independent of radiation fluxes. Extraneous high-energy spectral impurities, i.e., plasma emission, are likewise not responsible for redox reactivity since the use of optical filters to remove these components had no effect upon measured $\Phi_{\text{Co(II)}}$ values.

Direct excitation of the Cu(d) \rightarrow L(π^*) transition in the visible region might account for the low level of redox reactivity observed. Since electron transfer resulting from population of the charge-transfer state proceeds with near unitary efficiency, $\Phi \approx 0.5$, only ca. 0.1% of the total photons need be absorbed into this band at 514 nm; this will occur if $\epsilon_{514}(\text{Cu} \rightarrow \text{L}) \approx 0.6$. The Cu \rightarrow L bands are relatively broad ($\epsilon_{\text{max}} \approx 10^3$, $f(\text{oscillator strength}) \approx 0.04\text{--}0.1$)⁴ so that tailing to this extent into the visible region seems acceptable. The best evidence for this interpretation is the decreasing apparent $\Phi_{\text{Co(II)}}$ values with increasing wavelength measured across the breadth of cobalt ligand field band in Ro-vinylacetato-Cu(I) ion; the relative absorbance of the charge-transfer tail would be expected to decrease in the same way. The relative reactivities of other RoLCu^I ions appear somewhat inconsistent with this suggestion, however. One would expect at least some rough inverse correlation of $\Phi_{\text{Co(II)}}$ with frequency maxima of the Cu \rightarrow L bands, hence, extent of overlap in the visible region (cf. Figure 1), but none is found (Table I).³⁰ Likewise, irradiation of the systems containing amine bridging ligands at 488 nm should give greater reactivity than the corresponding nonconjugated alkenoates (which have identical charge-transfer frequency maxima) irradiated at 514 nm, contrary to observed behavior.

It is possible that reaction is initiated principally by excitation to cobalt(III) ligand field states. In this case, rationalization of the wavelength dependence of $\Phi_{\text{Co(II)}}$ requires postulation that either reactivity is a function of vibrational excitation or of the relative population of component electronic states in the first d-d band. (The nonequivalence in the ligand field of carboxylatopentaamminecobalt(III) ions gives rise to tetragonal distortion from octahedral geometry, splitting the 1T_1 and 1T_2 excited states.³¹) Both suggestions run counter to experience in organic photochemistry.⁵ However, observation of comparable wavelength dependencies in ligand-field photoaquations of RoL ions has been reported²⁰ as has evidence favoring inefficient internal con-

version between excited states in other nd^6 systems.³² It might be noted that, irrespective of considerations of geometrical distortions accompanying thermal equilibration of excited states, cobalt(III) ligand field excited states should be more reactive toward electron transfer than the ground state ions. Excitation corresponds to $t_{2g}^6 \rightarrow t_{2g}^5 e_g$ redistribution of electrons providing a π -symmetry acceptor "hole" for the incoming electron³³ and potentially significant spin conservation restrictions are removed if reaction occurs from triplet excited states.³⁴

Ligand Isomerization and Electron Transfer. Maleate-fumarate isomerization attending electron transfer is a topic with considerable history in the study of transition metal ion redox reactions. Early reports of substantial trans isomerization of ligand in reductions of Ro-maleate ion³⁵ have been thoroughly repudiated;¹⁴ despite the lack of detectable isomerization relative rate arguments have been advanced to support a mechanism involving a radical-anion intermediate, formation of which is thought to be rate determining.¹⁴ Our observation of highly efficient isomerization of Cu(I)-maleate ion from charge-transfer excited states possessing considerable radical anion character is consistent with this interpretation, i.e., radical anion intermediates, if they exist in the thermal electron transfer reaction, must necessarily have extremely short lifetimes. The absence of detectable isomerization in the photocatalyzed reaction of Ro-maleate-Cu(I) ion suggests as well that the intramolecular electron transfer step occurs at a rate considerably faster than the lower limit, $k \geq 10^7 \text{ sec}^{-1}$, which can be estimated from the radiative lifetime of the $Cu(d) \rightarrow L(\pi^*)$ singlet state.³⁶

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- (23) Mechanisms comprising facilitation of intersystem crossing to, e.g., the ligand-to-cobalt triplet (LMCT) state arising from spin-orbit interactions involving bound Cu(I) which might account for the enhanced reactivity of the binuclear ions can apparently be ruled out from similar studies with Ag(I) binding. Quantum yields for photoredox decomposition of Ro-vinylacetate ion, (RoL) = $2 \times 10^{-3} M$, resulting from charge-transfer excitation were unchanged by the presence of 1.0 M $AgClO_4$ and Ro-fumarate ion, (RoL) = $5 \times 10^{-3} M$, in 1.0 M $AgClO_4$ underwent no redox decomposition when irradiated at the L_2 band maximum (350 nm). Under these conditions appreciable binding of Ag(I) to the olefin bond undoubtedly occurs;¹⁹ binding does not perturb the cobalt(III) spectral properties. Heavy metal complexation therefore gives no indication of altering the kinetics of the photophysical-photochemical deactivation processes.
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