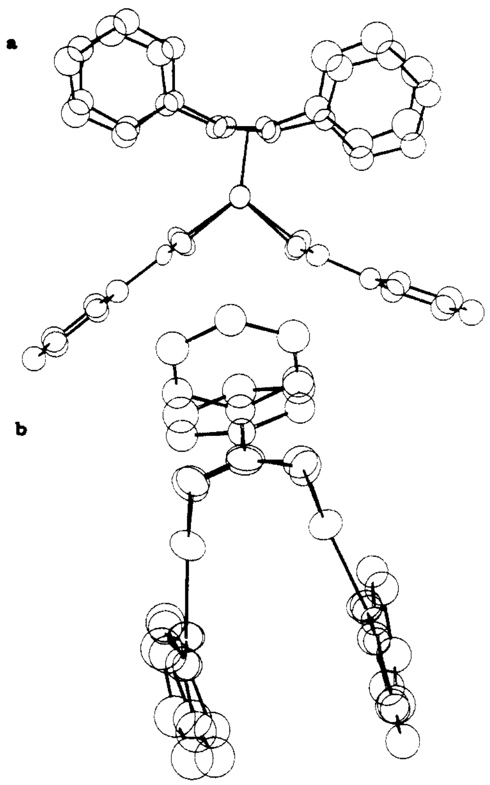

Figure 2. Projection of molecule 1 of complex II directly down (a) the Cu-Cu vector and (b) the C1≡C2 triple bond.

was carried out into the presence of a nitrogen base, since the formation of the corresponding carboxylic acids inhibited the reaction.[2] This is justified by the fact that the hydrogenation promoted by copper(I) is usually viewed as the consequence of the heterolytic splitting of the H_2 molecule. This process is enhanced by the presence of a basic substance, which plays a fundamental role in copper-based hydrogenation systems. In the absence of any added base, the oxygen atoms of the benzoato group can act as basic sites, benzoic acid being formed in many hydrogenation reactions of copper(I) benzoato complexes.[22]

In spite of this, the absorption of H_2 by complex II in the presence of quinoline decreases rather than increases. This unexpected result can be ascribed to a difference in the mechanism of hydrogenation of such different substrates. Molecules like *p*-benzoquinone may involve the oxidation of copper(I) to copper(II), so that the function of molecular hydrogen is to reduce the oxidation state of the metal acting as primary reducing agent of the organic molecule. Such a mechanism is unlikely in case of substrates like acetylenes, which do not cause the oxidation of the metal.

Acknowledgment. This work was supported by the CNR (Rome).

Registry No. II, 82808-26-2; III, 82808-27-3; $Cu(PhCO_2)$, 14604-51-4; PhC≡CPh, 501-65-5; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes and Table SI, listing anisotropic and isotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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Chromium(IV)-Induced Carbon-Carbon Bond Scission

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Received January 6, 1982

Induced electron-transfer reactions, in which a Co^{III}-bound organic ligand suffers a net two-electron oxidation initiated by an external oxidant such as Ce(IV), yielding a carbon radical intermediate, have been studied in detail by Taube and co-workers.[1] The cation radical formed subsequently undergoes an intramolecular second one-electron transfer, resulting in the reduction at the Co(III) center without altering the carbon skeleton of the ligand, except in case of Co^{III}-bound oxalato.[2] The extension of this work to Ce(IV) oxidation of Co(III) complexes of the α-hydroxy acids lactic, mandelic, and benzilic acids[3] showed no evidence for partition of the intermediate, even when the Ce(IV):Co(III) ratio taken exceeded 20:1, and the results are consistent with a mechanism in which electron transfers to the oxidants and C-C fission are synchoronous or nearly so.

The present note concerns the highly reactive oxidant Cr(IV), which is known to resemble Ce(IV) in reactivity.[4] We are interested in the oxidation of lactic, mandelic, benzilic, 2-hydroxy-2-ethylbutyric and 2-hydroxy-2-methylbutyric acid complexes of $(H_3N)_5Co^{III}$ in aqueous perchlorate. Though the oxidation of alcohols[5,6] and of aliphatic and aromatic aldehydes[7] by Cr(IV), generated by the reaction of Cr(VI) and V(IV),[8] has been extensively studied, this appears to be the first time this system has been employed for an induced electron-transfer reaction involving Co(III) complexes, with ligands in which the reaction centers are separated by a saturated fragment and should necessarily involve the breakage of a carbon-carbon bond.

Experimental Section

Vanadium(IV) perchlorate solution was prepared by the method of Espenson[8] using vanadyl sulfate (Alfa Product) and barium perchlorate (Alfa). Solutions of VO_2ClO_4 were prepared by dissolving V_2O_5 in 1 M $HClO_4$ overnight. Potassium dichromate (AR) was used

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Table I. Kinetic Data for the Reaction of Cr(IV) with Pentaamminecobalt(III) Complexes[a,e]

$10^3 \times$ [V(IV)], M	$10^5 \times$ [Co(III)], M	$10^2 k_1$,[f] s^{-1}	$10^3 \times$ [V(IV)], M	$10^5 \times$ [Co(III)], M	$10^2 k_1$,[f] s^{-1}
2.0		1.6	2.0	7.6[c]	1.6
4.0		5.7	2.0	15[c]	1.5
2.0		1.1[g]	2.0	6.7[d]	1.6
2.0	1.5[b]	1.5	2.0	13[d]	1.5
2.0	3.0[b]	1.6			

[a] Reactions were carried out at 25 °C with V(IV) in excess in the presence of V(V) and $[HClO_4] = 0.050$ M. [b] L = lactato. [c] L = mandelato. [d] L = benzilato. [e] Exponential curves are obtained in the presence of $[V(V)] = 7.8 \times 10^{-5}$ M (unless otherwise mentioned). [f] The pseudo-first-order specific rate. $k_1 = -d \ln [Cr(VI)]/dt$. [g] $[V(V)] = 12 \times 10^{-5}$ M.

without further purification. The concentrations of V(IV), V(V), and Cr(VI) were determined spectrophotometrically.[8] The Co(III) complexes of lactic and benzilic acids were prepared as their perchlorates as described by Butler,[9] and the corresponding derivatives of mandelic, 2-hydroxy-2-ethylbutyric (HEBA), and 2-hydroxy-2-methylbutyric (HMBA) acids by the method of Fan.[10] The specific rates for disappearance of Cr(VI) were estimated, with use of either a Beckman 5260 recording spectrophotometer or a Carl-Zeiss VSU2 spectrophotometer, by following the decrease in absorbance at 372 nm. In a typical experiment, the initial concentrations of reagents used were as follows: $[V(V)] = 7.8 \times 10^{-5}$ M, $[V(IV)] = 2.0 \times 10^{-3}$ M, $[Cr(VI)] = 2.2 \times 10^{-5}$ M, and $[Co(III)] = (6.7\text{–}13.4) \times 10^{-5}$ M in 0.050 M $HClO_4$. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Co(II) was estimated after the completion of reaction in the presence of excess V(IV) and V(V) formed during the reaction, by diluting 10-fold with concentrated HCl, allowing evolution of Cl_2 to cease, and then measuring the absorbance at 692 nm ($\epsilon = 560$).[11] Optical density measurements with blank solutions containing V(IV) and V(III) have been made to apply suitable corrections that come to about 20% of the total OD when $[V(IV)]_0 = 8.1 \times 10^{-3}$ M. Separate experiments with either V(V) and Co(III) or Cr(VI) and Co(III) yielded considerable amounts of Co(II) when the ligands were mandelato and lactato. With Cr(VI) and the Co(III)–benzilato complex alone, Co(II) is formed when the solution is left overnight, making the product analysis difficult. Though either Cr(VI) or V(V) reacts with the Co(III) complexes of lactic and mandelic acids, the reaction is rather slow compared to Cr(IV) oxidation of these compounds, and the competing oxidation becomes significant only when [Co(III)] is greater than the [Cr(VI)] as the excess unreacted Co(III) complex can react with V(V) formed, slowly, yielding more Co(II). The Co(II) estimated is, therefore, taken as a measure of Cr(IV) reaction with the Co(III) complex only in those cases where neither Cr(VI) nor V(V) yields Co(II), with Co(III). This is the case only with the Co(III) complexes of HEBA and HMBA. Because of the low absorptivity and volatility of butanone and acetone, attempts to estimate these ketones were unsuccesful.

Results and Discussion

Representative kinetic data, regarding the Cr(IV) oxidation of Co(III) complexes of mandelic, lactic, and benzilic acids, have been summarized in Table I. The rate of the reaction depends very nearly on the $[V(IV)]^2$, the first power of [Cr(VI)], and the inverse first power of [V(V)]. These results are in agreement with Espenson's work,[8] and the rate law corresponds to

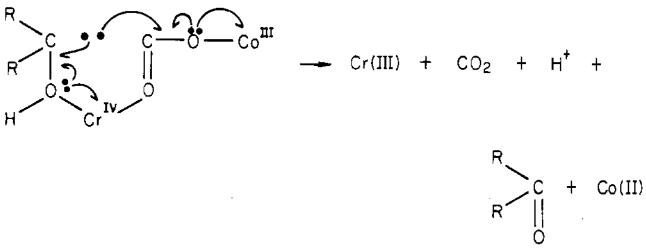
$$\text{rate} = k[Cr(VI)][V(IV)]^2/[V(V)] \tag{1}$$

Table II. Cr(IV) Oxidation of $[(H_3N)_5Co^{III}\text{–}L]^{2+}$ Compounds: Yields of Co(II)[f,g]

$(H_3N)_5Co^{III}$ complex	$[Co(III)]_0$, mM	[V(IV)], mM	[Cr(VI)], mM	[Co(II)], mM (%)
mandelato[a,b]	0.88	8.1	1.32	0.85[c] (96)
	1.20	8.1	1.32	1.14[c] (98)
2-hydroxy-2-ethylbutyrato[d]	3.5	20	0.88	0.40[e] (45)
	3.5	8.1	0.88	0.42[e] (46)
	1.5	8.1	0.88	0.44[e] (50)
2-hydroxy-2-methylbutyrato[d]	3.5	20	0.88	0.44[e] (50)
	3.5	8.1	0.88	0.45[e] (51)
	1.5	8.1	0.88	0.46[e] (52)

[a] Reaction carried out at 25 °C in 1 M $HClO_4$. [b] When $[Co^{III}\text{–mandelato}] > [Cr(VI)]$, yield of Co(II) exceeds $[Cr(VI)]_0$, as either V(V) or Cr(VI) can oxidize the unreacted Co(III). [c] Yield of Co(II) on the basis of $[Co(III)]_0$. [d] At 25 °C in 0.050 M $HClO_4$. [e] As neither Cr(VI) nor V(V) oxidizes the Co(III) complex, Cr(VI) is taken in deficiency and the yield of the product is calculated on the basis of $[Cr(IV)]_{formed} = [Cr(VI)]_0$. [f] Amount of Co(II) formed in 1 M $HClO_4$, by the reaction of 1.4×10^{-3} M Cr(VI) and 1.05×10^{-3} M Co^{III}–mandelato, comes to about 5% of the total yield and, with the reaction of 4.0×10^{-3} M V(V) and 1.05×10^{-3} M Co^{III}–mandelato, comes to about 20% of the total yield (the reaction mixture is quenched in concentrated HCl after 9 half-lives–after 6 min). [g] The results included in the table are at least an average of two independent runs.

Scheme I



The reaction is independent of Co(III) concentration as well as the change in structure of the ligands bound to Co(III). Similar observations have been made by Roček in the Cr(IV) oxidation of aromatic aldehydes.[7] The above kinetic picture can be explained by the following reaction sequence wherein the slow step is assumed to be the conversion of Cr(V) to Cr(IV) (there is a presumed change in coordination number from 4 to 6 during this process).[5,8,12]

Probably the oxidation of the Co(III) complex by Cr(IV) is involved in a subsequent fast step, resulting in a zero-order dependence on the substrates:[13]

$$Cr(VI) + V(IV) \rightleftharpoons Cr(V) + V(V)$$

$$Cr(V) + V(IV) \xrightarrow{\text{slow}} Cr(IV) + V(V)$$

$$Cr(IV) + V(IV) \rightarrow Cr(III) + V(V) \quad \text{(rapid)}$$

$$Cr(IV) + Co^{III}\text{–}L \rightarrow Co^{III}\text{–}L\cdot + Cr(III) \quad \text{(rapid)}$$

$$Co^{III}\text{–}L\cdot \xrightarrow[e^- \text{ transfer}]{\text{intramolecular}} Co(II) + \text{oxidized ligand} \quad \text{(rapid)}$$

According the above reaction scheme, $(H_3N)Co^{III}\text{–}L^{2+}$ competes with V(IV) for Cr(IV), and this may result in decrease in either V(V) produced or Co(II) produced in the last step. Table II summarizes the yield of Co(II) estimated in the Cr(IV) oxidation of the Co(III) complexes. The stoichiometric results are probably in keeping with the above reaction scheme in which $(H_3N)Co^{III}\text{–}L^{2+}$ intercepts the Cr(IV)–V(IV) reaction. As mandelic acid is a powerful reductant compared to

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(13) In preliminary experiments with either V(V) or Cr(VI) and Co(III) complexes, a first-order dependence on Co(III) was observed, in agreement with the present assumption that in a mixture of Cr(VI), V(IV), and Co(III), neither Cr(VI) nor V(V) is an oxidant for the ligand bound to Co(III).

HEBA or HMBA, the interception is more effective, yielding greater percentage of Co(II) whereas the ligands, HEBA and HMBA, probably react more slowly with Cr(IV) than does V(IV).[14]

As the Co(III) center is separated from the hydroxyl group by a saturated fragment, Cr(IV) oxidation necessarily occurs first at the hydroxyl center, generating a radical that should collapse with C–C fission and one-electron transfer to Co(III), occurring synchronously or very nearly so, resulting in the formation of Co(II) (Scheme I).[15,16]

Acknowledgment. The author wishes to thank Professor E. S. Gould, Kent State University, for the award of the postdoctoral fellowship, during 1979–1981, when part of this work was done.

Registry No. Cr, 7440-47-3; $[(H_3N)_5Co^{III}(lactato)]^{2+}$, 34464-03-4; $[(H_3N)_5Co^{III}(mandelato)]^{2+}$, 73543-61-0; $[(H_3N)_5Co^{III}(benzilato)]^{2+}$, 47253-58-7; $[(H_3N)_5Co^{III}(HEBA)]^{2+}$, 83174-77-0; $[(H_3N)_5Co^{III}(HMBA)]^{2+}$, 83174-78-1.

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(14) Under the reaction conditions either Cr(VI) or V(V) oxidizes the Co^{III}–mandelato complex but not the Co^{III}–HEBA or Co^{III}–HMBA complex at any considerable rate. Also, either Cr(VI) or V(V) oxidizes mandelic acid at a faster rate than either HEBA or HMBA. Hence, a similar order of reactivity is assumed for Cr(IV) also.

(15) Though no kinetic evidence for complex formation has been obtained, the mechanism proposed is similar to that proposed for the Ce(IV) oxidation of the same compounds.[3]

(16) Similar Fe(III)-induced electron transfer on C-bound Cr(III)–α-hydroxy acid complexes leads to the formation of Fe^{2+} and Cr^{2+}: Espenson, J. H.; Bakac, A. *J. Am. Chem. Soc.* **1980**, *102*, 2488.

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Photooxidation of Bis(maleonitriledithiolate) Complexes, $[M(S_2C_2(CN)_2)_2]^{2-}$ (M = Ni, Pd, Pt, Co, Cu)[1]

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Received February 24, 1982

Although transition-metal dithiolene complexes have been extensively investigated,[2] the photochemistry of these complexes has received little attention. The presence of intense UV–visible absorption bands and the accessibility of two or more oxidation states suggests that dithiolene complexes should display interesting redox photochemistry. Several recent reports substantiate this expectation.[3–6] Photooxidation of dithiolene complexes[3] and mixed diimine–dithiolene complexes[4,5] has been observed. Additionally, several bis(dithiolene) complexes were shown to catalyze photochemical H_2 production in H_2O/tetrahydrofuran mixtures.[6] This latter result suggests that transition-metal dithiolenes may ultimately prove useful in solar energy conversion. Some progress has been reported in identifying the reactive excited states. Vogler and Kunkely suggested that reaction occurs from a charge-transfer-to-solvent (CTTS) state in the photooxidation of the 1,2-dithiolene complexes $M(S_2C_2R_2)^Z$ (M = Ni, Pd, Pt, R = CN, Z = 2–; M = Ni, R = C_6H_5, Z = 1–) in chloroform.[3] We have also investigated the photochemistry of maleonitriledithiolate (mnt) complexes in chlorocarbon solutions under somewhat different conditions. One-electron oxidation was observed for each complex, with strongly wavelength-dependent quantum yields, but our results differ significantly from those of Vogler and Kunkely and indicate that additional excited states are reactive.

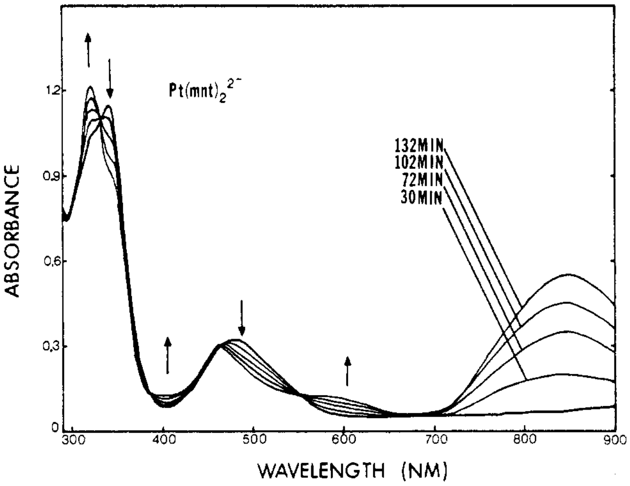

Figure 1. Electronic absorption spectral changes during 254-nm photolysis of $Pt(mnt)_2^{2-}$ in $CHCl_3/CH_3CN$ (24:1 v/v) at 23 °C. Isosbestic points appear at 540, 435, 395, and 315 nm.

Table I. Quantum Yields in 24:1 $CHCl_3/CH_3CN$[a]

complex	wavelength[d] 405	365	300	254	$E_{1/2}$[b]
$Ni(mnt)_2^{2-}$	7.3×10^{-4}	5.9×10^{-3}	0.096	0.71	+0.23
$Pd(mnt)_2^{2-}$	5.6×10^{-4}	3.3×10^{-3}	0.071	0.49	+0.46
$Pt(mnt)_2^{2-}$		0.046[c]	0.065	0.52	+0.21
$Co(mnt)_2^{2-}$	1.6×10^{-3}	7.5×10^{-3}	0.11	0.58	+0.05
$Cu(mnt)_2^{2-}$		4.0×10^{-3}		1.0	+0.34

[a] Quantum yields were reproducible within ±10%. [b] In volts vs. SCE in CH_3CN.[2a] [c] Measured at 335 nm. [d] All wavelengths are given in nm.

Experimental Section

Reagent grade chemicals were used without further purification. $PdCl_2$ and $PtCl_2$ were obtained from Alfa and used as received. All other metal salts were from J. T. Baker. Sodium maleonitriledithiolate was purchased from Strem Chemical and used as received or synthesized by literature methods.[7] All photochemical experiments were carried out in spectrophotometric grade solvents from Aldrich. Tetrabutylammonium salts of $Co(mnt)_2^{2-}$, $Cu(mnt)_2^{2-}$, $Pd(mnt)_2^{2-}$, and $Pt(mnt)_2^{2-}$ and the tetraethylammonium salt of $Ni(mnt)_2^{2-}$ were synthesized as previously described.[7] Satisfactory melting points, elemental analyses (Galbraith Laboratories), and UV–visibile absorption spectra were obtained for all the complexes.

Quantum Yields. Irradiations were performed at room temperature with an Ealing Stabilarc 250 system equipped with a 200-W Osram medium-pressure mercury-arc lamp. Wavelength selection was made with appropriate interference filters (Oriel) or with an Oriel 7240 monochromator set for a 10-nm band-pass. Lamp intensities were determined with use of ferrioxalate actionmetry for λ < 440 nm[8] and Reinecke's salt actinometry for longer wavelengths.[9] Reactions were monitored with a Cary 219 spectrophotometer. Quantum yields were calculated by using extinction coefficients for the intense near-IR band of the product monoanions[2] except for $Pd(mnt)_2^-$ and $Cu(mnt)_2^-$. For these complexes Δε at 440 and 460 nm, respectively, was measured and used to calculate quantum yields. The fraction of incident light absorbed was generally ~1, but corrections were applied as necessary.

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(1) Presented in part at the 182nd National Meeting of the American Chemical Society, New York, Aug 1981.

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