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Contribution from the Department of Chemistry,
Brookhaven National Laboratory, Upton, New York 11973

Cobalt(I) Polypyridine Complexes. Redox and Substitutional Kinetics and Thermodynamics in the Aqueous 2,2'-Bipyridine and 4,4'-Dimethyl-2,2'-bipyridine Series Studied by the Pulse-Radiolysis Technique[1]

HAROLD A. SCHWARZ,* CAROL CREUTZ, and NORMAN SUTIN

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Pulse radiolysis was used to study Co(I) produced by e_{aq}^- reduction of Co(II) in aqueous solutions containing 2,2'-bipyridine (bpy) or 4,4'-dimethyl-2,2'-bipyridine (dmb) and a hydroxyl radical scavenger. Six equilibria between CoL_n^+ and CoL_n^{2+} pairs were characterized. The absorption maxima and stability constants (log *K*) of the CoL_n^+ species are as follows: $Co(bpy)_3^+$, 610 nm, 6.9; $Co(bpy)_2^+$, 570 nm, 7.6; $Co(bpy)^+$, 670 nm, ≥12; $Co(dmb)_3^+$, 610 nm, 7.3; $Co(dmb)_2^+$, 500 nm, 8.0; $Co(dmb)^+$, 660 nm, ≥12. The reduction potentials vs. NHE, based on $E°(Co(bpy)_3^{2+/+}) = -0.95$ V and $E°(Co(dmb)_3^{2+/+}) = -1.07$ V, were as follows: $Co(bpy)_2^{2+/+}$, −1.09 V; $Co(bpy)^{2+/+}$, −1.23 V; $Co(dmb)_2^{2+/+}$, −1.17 V; $Co(dmb)^{2+/+}$, −1.29 V; $Co^{2+/+}$, ≤−1.6 V. Stability constants were also measured for the Co(II) species in 0.1 M chloride. The log *K* values are 5.95, 5.27, and 4.60 for $Co(bpy)^{2+}$, $Co(bpy)_2^{2+}$, and $Co(bpy)_3^{2+}$, respectively, and 6.38, 5.92, and 5.25 for $Co(dmb)^{2+}$, $Co(dmb)_2^{2+}$, and $Co(dmb)_3^{2+}$, respectively. The $(CH_3)_2\dot{C}OH$ and $CO_2^-\cdot$ radicals, produced by ·OH oxidation of 2-propanol and formate, react slowly ($k \sim 10^6$ to 4×10^7 M^{-1} s^{-1}) with the Co(II) complexes to yield Co(I) and radical-addition products in parallel.

Introduction

Cobalt(I) polypyridine complexes have recently been implicated as intermediates in systems effecting the homogeneous photoreduction of water to H_2[2-4] and of carbon dioxide to CO.[5] Although the earlier literature reveals relatively few studies[6-9] of these complexes containing chelating aromatic amines such as 2,2'-bipyridine (bpy), great effort has gone into the characterization of Co(I) complexes (the oximes) related to vitamin B_{12} and has established the interesting and valuable potential catalytic applications of such species.[10-12] The bulk are powerful reducing agents and nucleophiles as are the "organometallic" cobalt(I) complexes containing, e.g., carbonyl, phosphine, etc., ligands.[13]

Our interest in the cobalt(I) polypyridine complexes originated with their application in homogeneous water photoreduction.[2,3] In an effort to identify the cobalt species responsible for water reduction, we have conducted flash-photolysis, pulse-radiolysis, and other experiments. The CoL_3^+ species are high-spin d^8 complexes[6-9] that can be isolated as solids and studied in solutions made from the solids. Indeed, recent X-ray crystallographic work establishes that $Co(bpy)_3^+$ is a traditional tris-chelated complex containing six metal-nitrogen bonds.[14] However, under the conditions of catalytic interest, complexes of lower bipyridine content (mono and bis complexes) are produced in addition to the tris complex. As these species may undergo interconversion and/or oxidation on a very short time scale, the pulse-radiolysis technique has proven the method of choice for their study. All the Co(I) complexes absorb strongly in the visible region ($\epsilon > 10^3$ M^{-1} cm^{-1}, 550-650 nm) so that they are readily studied in the presence of large excesses of their Co(II) counterparts, which absorb negligibly above ~400 nm. Here we report the spectra of the CoL_n^+ species (L = bpy, 4,4'-dimethyl-2,2'-bipyridine (dmb); *n* = 1-3) and the equilibrium and rate constants for their interconversion via electron-transfer reactions with CoL_n^{2+} complexes. (Coordinated water molecules are omitted for the sake of brevity.) Our studies show that cobalt(I) has a very high affinity for bipyridine and that the cobalt(II)-cobalt(I) couples (CoL_2^{2+}-CoL_2^+, etc.) readily undergo electron exchange.

Table I. Co(II) Stability Constants (0.1 M KCl, 23 ± 2 °C)

eq no.	reaction	log *K*	
		bpy	dmb
1	$Co^{2+} + L \rightleftharpoons CoL^{2+}$	5.95	6.38
2	$CoL^{2+} + L \rightleftharpoons CoL_2^{2+}$	5.27	5.92
3	$CoL_2^{2+} + L \rightleftharpoons CoL_3^{2+}$	4.60	5.25
4	$H^+ + L \rightleftharpoons LH^+$	4.42	5.35

Experimental Section

Puratronic $CoSO_4$ was purchased from Johnson-Matthey, 2,2'-bipyridine from Fisher, and 4,4'-dimethyl-2,2'-bipyridine from G. F. Smith. UV grade *n*-hexane was used, and all other chemicals were reagent grade. The dmb and bpy used in the measurement of Co(II) stability constants were recrystallized several times from *n*-hexane to remove an impurity that absorbed at 320 nm. The bpy was analyzed by potentiometric titration with HCl. The dmb was analyzed by dissolving the base in a slight excess of 0.1 M HCl and back-titrating to near constant pH, which occurs when dmb starts to precipitate. Stock $CoSO_4$ solutions were evaporated to dryness, and the residue was weighed to establish $CoSO_4$ content.

The solution for pulse radiolysis was prepared in a 60-mL bubbler attached to the pulse-radiolysis cell. A 50-mL portion of $CoSO_4$ solution containing all components except bpy or dmb was deaerated with argon; then, the appropriate amount of bpy or dmb was added and the pH adjusted with NaOH or H_2SO_4, while the solution was bubbling. This procedure was used because Co(II)-L solutions are O_2 sensitive.

The pulse-radiolysis equipment has been described previously.[15] A 6-cm light path was used, and the radiation dose was in the range of 0.5 × 10^{-6} to 3 × 10^{-6} M total radicals/pulse. There was often slight oxidation of the solution before pulsing, evidenced by rapid oxidation of Co(I) on the first one or two pulses. Subsequent pulses, up to at least 15 pulses of 10^{-6} M radicals each, gave consistent results.

Results

Stability Constants of the CoL_n^{2+} Complexes. The bpy and dmb cobalt(II) complexes can be prepared by simply mixing Co^{2+}

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Table II. Hydrated-Electron Yield Dependence on Ethanol and Phosphate Buffer (pH 10) Concentrations

$[C_2H_5OH]$, M	[buffer], M	G^a	$[C_2H_5OH]$, M	[buffer], M	G^a
0	0	2.65^b	0.42	0	3.07
0.04	0	2.89	0	0.02	2.83
0.19	0	3.02	0.50	0.02	3.44

^{a} Yield per 100 eV of absorbed energy. ^{b} Reference 19c.

solutions with ligand solutions. Equilibration is expected to be complete in about 1 s. The compositions of the solutions are determined by four equilibria:

$$Co^{2+} + L \rightleftharpoons CoL^{2+} \tag{1}$$

$$CoL^{2+} + L \rightleftharpoons CoL_2^{2+} \tag{2}$$

$$CoL_2^{2+} + L \rightleftharpoons CoL_3^{2+} \tag{3}$$

$$L + H^+ \rightleftharpoons LH^+ \tag{4}$$

Several values, which differ by factors up to 2, have been reported[16,17] for the stability constants of Co(II)–bpy complexes, but none are available for dmb complexes. We have determined the constants for dmb complexes and redetermined those for bpy complexes by the solvent partition method, with *n*-hexane as the second phase. The technique is similar to that used by Irving and Mellor[16] with the following differences: The Co(II) concentration was 10^{-3} M; The solutions were not thermostated (but remained at 23 ± 1 °C); All solutions were deaerated with argon before mixing, in order to prevent oxidation of the Co(II). Ionic strength was maintained at 0.10 M with KCl. The following parameters were determined: The molar absorptivities for the free ligands in aqueous solution are 1.36×10^4 M^{-1} cm^{-1} at 280 nm for bpy (lit.[16] 1.30×10^4) and 1.30×10^4 M^{-1} cm^{-1} at 279 nm for dmb. In *n*-hexane the molar absorptivities are 1.50×10^4 M^{-1} cm^{-1} at 282 nm for bpy (lit.[16] 1.45×10^4) and 1.51×10^4 M^{-1} cm^{-1} at 280 nm for dmb. The distribution coefficients (*n*-hexane to 0.1 M KCl) were 9.3 for bpy (lit.[16] 9.6) and 67 for dmb. The stability constants found are given in Table I. The values of K_4 are in good agreement with literature values, but K_1, K_2, and K_3 for bpy are higher, lower, and lower, respectively, than most literature values by 25–50%. The large scatter in the values is possibly explained by air oxidation of Co(II) in earlier work. In any event, the values in Table I have been used for subsequent data analysis.

Note that the three $Co(bpy)_n^{2+}$ constants differ by a factor of 13. This means that, at $[L]/[Co(II)] < 3$, at least two cobalt(II) species will be present in substantial amounts and, in particular, CoL_2^{2+} cannot exceed 51% of the total Co(II). The unavoidable necessity of working with mixtures complicates the pulse-radiolysis studies.

Pulse-Radiolysis Yields. The radiolysis of water produces e_{aq}^- and OH radicals in about equal proportions and about 20–25% as much H atoms, H_2O_2, and H_2. The solutions that were irradiated in this work contained $CoSO_4$, ligand, buffer (acetate, phosphate, borate), and a scavenger for the OH radicals and H atoms, usually sodium formate or 2-propanol, or 2-methyl-2-propanol. It is known that OH radicals are very unreactive with Co^{2+} ($k = 2 \times 10^6$ M^{-1} s^{-1}),[18] but no measurements have been reported for reaction with the CoL_n^{2+} complexes. Addition of ·OH to the aromatic ligands is likely to be diffusion limited, and the ·OH-scavenger concentrations were adjusted to ensure that a negligible fraction of ·OH reacted with the Co(II) complexes (or other constituents of the solution).

The net yield of reduction of a solute by e_{aq}^- is relatively insensitive to the concentrations of reactants in solution but not completely so. In particular, high concentrations of alcohols increase the yield of e_{aq}^- available for reduction. Such effects arise from the fact that the radicals in radiolysis are produced in spurs, several pairs at a time, and combine to some extent while diffusing out of the spurs. The yields are rather sensitive to alcohols because e_{aq}^- reacts very rapidly with ·OH radicals but very slowly with the R· radicals that replace them at high alcohol concentration. In Table II the e_{aq}^- yields in the absence of e_{aq}^- reactants are given as a function of ethanol concentration. The yields were determined from the intensity of the e_{aq}^- absorption at 650 nm, 100 ns after the pulse of electrons, and are in good agreement with similar literature data for methanol[19] when compared at equivalent ·OH reactivity concentrations.

Table III. Rate Constants for Reduction of Cobalt(II) Complexes by the Hydrated Electron at 25 °C^a

eq no.	reaction	k, M^{-1} s^{-1}
5	$e_{aq}^- + Co^{2+} \rightarrow Co^+$	3.0×10^9 ^{b}
6	$e_{aq}^- + Co(bpy)^{2+} \rightarrow Co(bpy)^+$	3.5×10^{10}
7	$e_{aq}^- + Co(bpy)_2^{2+} \rightarrow Co(bpy)_2^+$	5.3×10^{10}
8	$e_{aq}^- + Co(bpy)_3^{2+} \rightarrow Co(bpy)_3^+$	7.4×10^{10}

^{a} Determined in 5×10^{-5} M Co(II) solutions with 0.005 M phosphate buffer, 0.15 M ethanol, and varying amounts of bpy. ^{b} Effective value for the medium given in footnote *a*. This value probably represents reaction with Co^{2+}–HPO_4^{2-} ion pairs since literature values[21] at low ionic strength are (1.0–1.2) × 10^{10} M^{-1} s^{-1}.

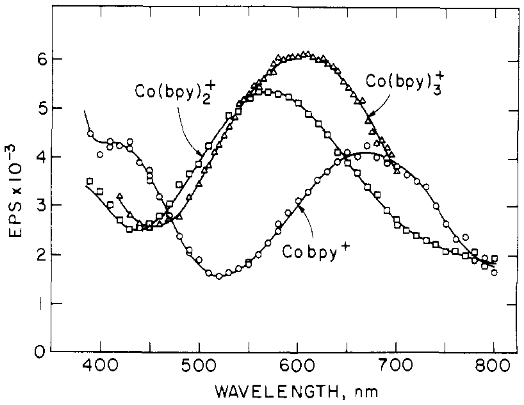

Figure 1. Absorption spectra of $Co(bpy)_n^+$ complexes. The ordinate is molar absorptivity (M^{-1} cm^{-1}).

The magnitude of the e_{aq}^- yield is important here only in the determination of the molar absorptivities of the CoL_n^+ species. These were determined in solutions containing 0.5 M 2-methyl-2-propanol. since 2-methyl-2-propanol reacts with ·OH with a rate constant of 5×10^8 M^{-1} s^{-1} while ethanol reacts at 1.7×10^9 M^{-1} s^{-1},[20] the 2-methyl-2-propanol is equivalent in reactivity to 0.15 M ethanol and the e_{aq}^- yield would be expected to be 3.0. The yield of reduction actually occurring will be slightly larger than this, however, because the CoL_n^{2+} concentrations are large (up to 0.005 M). An e_{aq}^- yield of 3.2 was assumed.

It should be noted that spur processes are complete in about 10^{-8} s and do not affect the rate studies reported here, which were all on time scales of 3×10^{-7} s or longer.

Production and Equilibration of Co(I) Complexes. The rate constants for reduction of $Co(bpy)_n^{2+}$ complexes by e_{aq}^- were measured by following e_{aq}^- decay at 650 nm in 5×10^{-5} M Co(II) solutions with 0.005 M phosphate buffer, 0.15 M ethanol, and varying amounts of bpy. The rate constant for reaction with Co^{2+} in the absence of bpy was found to be 3.0×10^9 M^{-1} s^{-1}. This value probably represents reaction with Co^{2+}–HPO_4^{2-} ion pairs, as literature values[21] at low ionic strength are (1.0–1.2) × 10^{10}

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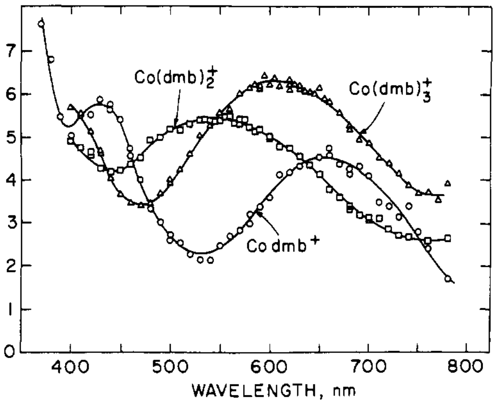

Figure 2. Absorption spectra of Co(dmb)$_n^+$ complexes. (The Co(dmb)$_2^+$ spectrum is not corrected for Co(dmb)$_3^+$, about 10%, produced at the same time.) The ordinate is molar absorptivity (M^{-1} cm^{-1}).

M^{-1} s^{-1}. The hydrated-electron reactions are presented in Table III. In the presence of bpy, the pseudo-first-order rate constant for the disappearance of e_{aq}^- is given by

$$k_{obsd} = k_6[Co(bpy)^{2+}] + k_7[Co(bpy)_2{}^{2+}] + k_8[Co(bpy)_3{}^{2+}] + k_5[Co^{2+}] + 2.5 \times 10^{10}[bpy]$$

The last two terms are small (the value of 2.5×10^{10} M^{-1} s^{-1} for reaction with bpy is from Mulazzani et al.[22a]), and so k_6, k_7, and k_8 can be determined from measurements of k_{obsd} at various bpy concentrations. The results are given in Table III.

Reaction of CoL$_n^{2+}$ ($n \neq 0$) with e_{aq}^- yields products (CoL$_n^+$) absorbing intensely in the visible region. At longer times and at higher Co(II) concentrations, the spectra observed at the end of the e_{aq}^- reduction undergo further changes due to equilibration reactions of Co(I) with the three CoL$_n^{2+}$ complexes. These reactions are observed with any of the OH radical scavengers present, but the data presented here were all obtained with 2-methyl-2-propanol as scavenger because it was found that the 2-methyl-2-propanol radical does not react appreciably with the Co(II) complexes. The appropriate CoL$_n^{2+}$ concentrations were kept sufficiently high for equilibrations to occur before second-order reactions (R· + Co(I)) could interfere.

In 0.04 M Co(II) solution with 3.2×10^{-4} M total bpy, the product of e_{aq}^- reduction is 90% Co$_{aq}^+$, which does not absorb in the wavelength range used here. The spectrum of Figure 1 labeled Co(bpy)$^+$ is developed with $k_{obsd} = 3.8 \times 10^5$ s^{-1}. In 3.6×10^{-3} M total bpy solution, this step is complete within 10^{-6} s and a further change is observed with $k_{obsd} = 2 \times 10^5$ s^{-1}, the resulting spectrum being close to that labeled Co(bpy)$_2^+$ in Figure 1. (The spectrum in Figure 1 has been corrected for the fact that the reaction is only 95% complete at equilibrium.) Last, in solutions with 5×10^{-3} M Co(II) and 2.7×10^{-3} M total bpy, the spectrum labeled Co(bpy)$_3^+$ is developed with $k_{obsd} = 3.0 \times 10^5$ s^{-1}. Similar results were obtained for dmb solutions, and the spectra are shown in Figure 2. Not shown in the figures are intense ($\Delta\epsilon \sim 1 \times 10^4$ M^{-1} cm^{-1}) CoL$^+$ bands at 340 and 335 nm for bpy and dmb, respectively. As noted above, the ϵ values given in Figure 1 are based on $G(e_{aq}^-) = 3.2$. The Co(bpy)$_3^+$ and Co(dmb)$_3^+$ molar absorptivities were also measured in more dilute solutions: 0.1 M 2-methyl-2-propanol and 5×10^{-4} M Co(II) with 1.1×10^{-3} M ligand, for which the cobalt(I) yield (2.9/100 eV) is more certain. The molar absorptivity found for Co(bpy)$_3^+$ at 610 nm (6200 M^{-1} cm^{-1}) is considerably greater than that found by earlier workers $\sim 1.6 \times 10^3$ M^{-1} cm^{-1},[8] but comparable to that (6800 M^{-1} cm^{-1}) determined for [Co(bpy)$_3$]Cl freshly dissolved in ethanol.[3]

Note that the CoL$_3^+$ spectra are observed even when the total [Co(II)] is twice the total [L]. In these solutions the distribution of Co(II) species is $[Co^{2+}] > [CoL^{2+}] \gg [CoL_2{}^{2+}] \gg [CoL_3{}^{2+}]$. The three equilibration steps leading to CoL$_3^+$ are electron-transfer reactions (eq 9–14). Each step was isolated in time by adjusting the total Co(II) and ligand concentrations so that $k_{obsd} > 3 \times 10^4$ s^{-1} and the previous step (if any) was at least 1 order of magnitude faster while the subsequent step was at least a factor of 30 slower. The kinetics observed were pseudo first order with

Table IV. Rate and Equilibrium Constants for Co(I)–Co(II) Reactions at 25 °C[a]

eq no.	reaction	$10^{-9}k_f$, M^{-1} s^{-1}	$10^{-6}k_r$, M^{-1} s^{-1}	K[b]
9	$Co^+ + Co(bpy)^{2+} \rightleftharpoons Co^{2+} + Co(bpy)^+$	1.2	$>10^6$ [c]	
10	$Co(bpy)^+ + Co(bpy)_2{}^{2+} \rightleftharpoons Co(bpy)^{2+} + Co(bpy)_2{}^+$	2.1	11	225
11	$Co(bpy)_2{}^+ + Co(bpy)_3{}^{2+} \rightleftharpoons Co(bpy)_2{}^{2+} + Co(bpy)_3{}^+$	2.0		200
12	$Co^+ + Co(dmb)^{2+} \rightleftharpoons Co^{2+} + Co(dmb)^+$	1.0		
13	$Co(dmb)^+ + Co(dmb)_2{}^{2+} \rightleftharpoons Co(dmb)^{2+} + Co(dmb)_2{}^+$	1.8	20	125
14	$Co(dmb)_2{}^+ + Co(dmb)_3{}^{2+} \rightleftharpoons Co(dmb)_2{}^{2+} + Co(dmb)_3{}^+$	2.5	75	(50)[d]

[a] At 0.2 M ionic strength unless otherwise stated. [b] Determined from the apparent molar absorptivities at the end of the equilibrium kinetics. [c] See ref 23. [d] At 0.1 M ionic strength.

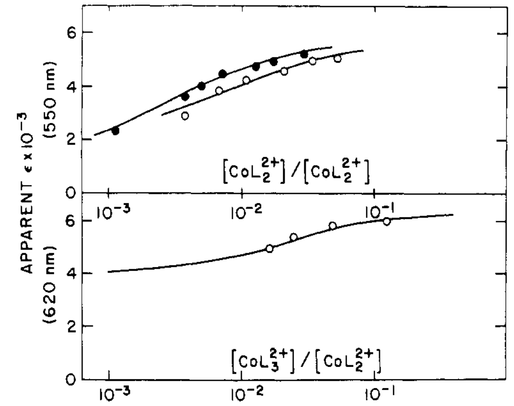

Figure 3 Apparent molar absorptivities (M^{-1} cm^{-1}) of CoL$_{n-1}^+$–CoL$_n^+$ mixtures as a function of the distribution of Co(II) complexes in solution. Top curves, CoL$^+$–CoL$_2^{2+}$ equilibria (eq 10, 13): ●, 0.05 M Co(II), bpy; ○, 0.05 M Co(II), dmb. Bottom curve, Co(dmb)$_2^+$–Co(dmb)$_3^{2+}$ equilibrium (eq 14) in 0.01 M Co(II). Conditions for all solutions: 0.01 M acetate buffer, 0.5 M 2-methyl-2-propanol, ionic strength 0.1–0.2 M.

$$k_{obsd} = k_f[CoL_n{}^{2+}] + k_r[CoL_{n-1}{}^{2+}]$$

and values of k_f and k_r (where available) are given for eq 9–14 in Table IV. For reaction 11, $k_r[CoL_2{}^{2+}]$ was negligibly small under the conditions used.

Equilibrium constants for reactions 10, 13, and 14 can be determined from measurements of the apparent molar absorptivities at the completion of the pseudo-first-order equilibration steps as a function of solute composition:

$$\epsilon_{app} = \frac{\epsilon_{n-1} + \epsilon_n K[CoL_n{}^{2+}]/[CoL_{n-1}{}^{2+}]}{1 + K[CoL_n{}^{2+}]/[CoL_{n-1}{}^{2+}]}$$

(where ϵ_{n-1} and ϵ_n are the molar absorptivities of CoL$_{n-1}$ and CoL$_n^+$). The data are given in Figure 3 along with calculated curves, and the equilibrium constants are given in Table IV. This method is reasonable for reactions 10 and 13 but not very accurate for reaction 14 since the molar absorptivities of Co(dmb)$_2^+$ and Co(dmb)$_3^+$ differ by only 30%. In addition, only data at higher [Co(dmb)$_3^+$]/[Co(dmb)$_2^+$] ratios were useable, since equilibration was too slow compared to radical–Co(I) reactions at lower ratios of CoL$_3^{2+}$ to CoL$_2^{2+}$. Thus, the K_{14} measurement is probably reliable to a factor of 2. The agreement of the equilibrium

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Table V. Equilibrium CoL_3^+/CoL_2^+ Ratios in 5 mM Co(II) Solutions as a Function of Total 2,2′-Bipyridine Concentration

$[bpy]_t$, mM	$[CoL_3^{2+}]/[CoL_2^{2+}]$	$[CoL_3^+]/[CoL_2^+]$			K_{11}
		610 nm	650 nm	680 nm	
1.0	0.010	1.4	1.5	1.7	150
1.7	0.019	5.7	4.1	4.6	260
2.0	0.023	5.3	4.9	5.9	230
4.4	0.073	10	13	19	190

constants with k_f/k_r values (within 20–50%) is satisfactory.

It was not possible to measure the equilibrium constant for reaction 11 in the above manner. At equilibrium the ratio $[Co(bpy)_3^{2+}]/[Co(bpy)_2^{2+}]$ is about 0.01, and $[Co(bpy)_3^{2+}]$ is too small for reaction 11 to be rapid at accessible Co(II) concentrations. At the Co(II) levels used, reaction occurs in about 10^{-3} s but is obscured by other reactions. At sufficiently large pH (>6) and after about 10^{-2} s, the other reactions are largely complete and f, the fraction of Co(I) present as CoL_2^+, can be determined from the ratio of the absorbance at wavelength λ to that at 550 nm, the isobestic point for CoL_2^+ and CoL_3^+:

$$R_\lambda \equiv A_\lambda/A_{550} = R_{\lambda,2}f + R_{\lambda,3}(1 - f)$$

($R_{\lambda,2}$ and $R_{\lambda,3}$ are the values of R_λ for CoL_2^+ and CoL_3^+, respectively, and are obtained from the spectra given in Figure 1.) The $[CoL_3^+]/[CoL_2^+]$ ratio is $(1/f - 1)$, and for bpy, K_{11} is $[CoL_3^+]/[CoL_2^+]$ divided by the $[CoL_3^{2+}]/[CoL_2^{2+}]$ ratio calculated from the stability constants of the Co(II) species and the solution composition. Data were collected at four wavelengths (550, 610, 650, 680 nm) for four Co(II)–bpy solutions and are presented in Table V. This method is not very precise, as $R_{\lambda,2}$ and $R_{\lambda,3}$ differ by only 20–30% in the 600–700-nm region. Lower bpy-to-Co(II) ratios are not usable since the solutions contain insufficient $Co(bpy)_3^{2+}$ to equilibrate the $Co(bpy)_n^+$. Thus, the value of K_{11} so obtained and given in Table IV is probably reliable to ±50%. Reactions 9 and 12 could not be studied in the presence of acetate buffer as Co^+ was observed to form an acetate complex. (This complex had negligible effect at the higher polypyridine concentrations used to study CoL_2^+.) In the absence of buffer the formation of $Co(bpy)^+$ was limited by the competition of reaction 9 with a first-order decay of Co^+. For instance, the $Co(bpy)^+$ absorbance at 660 nm in a solution containing 0.05 M Co^{2+} and 2.5×10^{-6} M $Co(bpy)^{2+}$, a ratio of 2×10^4 to 1, was only half that observed in more concentrated $Co(bpy)^{2+}$ solutions, but k_{obsd} for growth of $Co(bpy)^+$ was 4000 s^{-1} while that for decay of Co^+ in the absence of the $Co(bpy)^{2+}$ was 2000 s^{-1}. Thus the entire reduction in absorbance could be accounted for by the kinetic effect and $K_9 > 2 \times 10^4$. A more stringent limit of $K_9 \geq 10^6$ was determined from a study of other equilibria.[23]

Reactions of 2-Propanol Radicals and $CO_2^-\cdot$ with Co(II). The OH radicals produced in the pulse radiolysis react with 2-propanol to form 2-propanol radicals (R·) with a rate constant of 2×10^9 M^{-1} s^{-1}.[20]

$$\cdot OH + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O$$

(About 15% of the product is $CH_3COHCH_2\cdot$.[24]) The subsequent reaction of R· with CoL_n^{2+} was followed by the growth in absorbance at 430 nm as a function of total ligand and Co(II) concentrations. As was the case for e_{aq}^- reactions, the observed rates are linear combinations of reaction rates with each of the Co(II) species present. The individual rate constants for the various bpy and dmb complexes are given in Table VI (eq 15–20).

If the 2-propanol–radical reactions gave quantitative yields of CoL_n^+, then the ratio of the absorbance after the radical reaction to that before the reaction should be ~2:1 (the ratio of total radical yield to e_{aq}^- yield) at all wavelengths. Such was not the case. When [bpy]/[Co(II)] was 1, only a 10% increase in absorbance was seen at 600 nm (near the $Co(bpy)_3^+$ maximum) accompanied by the R· reaction although the absorbance nearly doubled at 430 nm. Evidently, radical addition to the coordinated bpy[22b] (or formation of some other radical adduct) is the main reaction, and the product has an absorption maximum near 430 nm. By contrast, as the ratio of total bpy to Co(II) is increased to between 2 and 3, the absorbance ratio at 600 nm approaches 2, indicating that R· reduces $Co(bpy)_3^{2+}$ to $Co(bpy)_3^+$. In order to estimate f_{n1}, the fraction of R·–CoL_n^{2+} reaction yielding CoL_n^+, R_{obsd}, the ratio of the yield of CoL_3^+ after and before the radical reaction, was monitored as a function of solution composition under conditions where CoL_3^+ was the dominant form at equilibrium. Conditions were such that CoL_3^+ formation via eq 9–11 was much more rapid than the R·–Co(II) reactions. The individual final-to-initial absorbance ratio at 600 nm, R_n, for reactions 15–20 can be determined by assuming that the observed ratio R_{obsd} is a linear combination of the individual ratios R_n weighted by f_{n2}, the fraction of total R· reaction with CoL_n^{2+}. (f_{n2} is determined by k_n for eq 15–20 and by the distribution of Co(II) complexes present.) Then the fraction of CoL_n^+ formed (all equilibrated to CoL_3^+ under these conditions) is simply $(R_n - 1)/1.1$. Product ratios determined in this way are given Table VI for eq 15–20.

Table VI. Rate Constants for Reaction of Cobalt(II) Complexes with the 2-Propanol Radical (R·) and Formate Radical $(CO_2^-\cdot)$[a]

eq no.	reaction	k,[b] M^{-1} s^{-1}
15	$R\cdot + Co(bpy)^{2+} \rightarrow Co(bpy)R^{2+}$	2.0×10^6
16	$R\cdot + Co(bpy)_2^{2+} \rightarrow Co(bpy)_2R^{2+}$	2.0×10^6
17	$R\cdot + Co(bpy)_3^{2+} \rightarrow Co(bpy)_3R^{2+}$ (40%) $\rightarrow Co(bpy)_3^+ + (CH_3)_2CO + H^+$ (60%)	4.0×10^7
18	$R\cdot + Co(dmb)^{2+} \rightarrow Co(dmb)R^{2+}$	1.0×10^6
19	$R\cdot + Co(dmb)_2^{2+} \rightarrow Co(dmb)_2R^{2+}$	1.0×10^6
20	$R\cdot + Co(dmb)_3^{2+} \rightarrow Co(dmb)_3R^{2+}$	5.0×10^6
21	$CO_2^-\cdot + Co(bpy)^{2+} \rightarrow Co(bpy)CO_2^+$	6.0×10^6
22	$CO_2^-\cdot + Co(bpy)_2^{2+} \rightarrow Co(bpy)_2CO_2^+$ (70%) $\rightarrow Co(bpy)_2^+ + CO_2$ (30%)	1.6×10^7
23	$CO_2^-\cdot + Co(bpy)_3^{2+} \rightarrow Co(bpy)_3CO_2^+$ (10%) $\rightarrow Co(bpy)_3^+ + CO_2$ (90%)	3.5×10^7
24	$CO_2^-\cdot + Co(dmb)^{2+} \rightarrow Co(dmb)CO_2^+$	1.1×10^7
25	$CO_2^-\cdot + Co(dmb)_2^{2+} \rightarrow Co(dmb)_2CO_2^+$	1.1×10^7
26	$CO_2^-\cdot + Co(dmb)_3^{2+} \rightarrow Co(dmb)_3CO_2^+$ (40%) $\rightarrow Co(dmb)_3^+ + CO_2$ (60%)	1.7×10^7

[a] Reactions 21–23 at 0.2 M ionic strength, 24–26 at 0.5 M ionic strength. [b] Total rate constant for R· or $CO_2^-\cdot$ consumption.

Very similar results were obtained for the reactions of $CO_2^-\cdot$ with the various CoL_n^{2+} species, and the results are given for eq 21–26 in Table VI. In addition, a 10^{-2} M Co(II) and 2×10^{-2} M dmb (total) solution was saturated with CO_2 at pH 5.7, and it was found that $Co(dmb)_3^+$ reacts with CO_2 with a rate constant of about 5×10^5 M^{-1} s^{-1} to give a product with an absorption maximum at 530 nm (molar absorptivity of 2700 M^{-1} cm^{-1}, if the reaction is quantitative).

Discussion

Magnetic[8,9] and structural[14] results are consistent with the formulation of $Co(bpy)_3^+$ as a six-coordinate, high-spin d^8 cobalt(I) complex. Its absorption spectrum features an intense band at 610 nm (Figure 1) and an equally intense band at even longer wavelengths (1390 nm).[8] The spectrum of $Co(dmb)_3^+$ is very similar, but with the low-energy band shifted to slightly longer wavelength (1490 nm).[8] These absorption bands have been attributed to metal-to-ligand charge-transfer transitions,[8] and their low energies are entirely consistent with the low Co(II)/Co(I) reduction potentials. By contrast, for the CoL_1^+ complexes a $Co(II)–L^-\cdot$ formulation is strongly implicated by the presence of intense absorption bands at ~340 nm (absent in the CoL_2^+ and CoL_3^+ spectra). These bands, taken with the ~430- and ~650-nm bands ($\epsilon \sim 5 \times 10^3$ M^{-1} cm^{-1}), are characteristic of

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(23) Unpublished studies of the reduction of $Ru(dmb)_3^{2+}$ to $Ru(dmb)_3^+$ by Co^+ ($K \geq 1.4 \times 10^4$) and by $Co(bpy)^+$ ($K = 0.012$) give an estimate of K_9 (the ratio of these two equilibrium constants).

(24) Asmus, K.-D.; Moeckel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

Table VII. Reduction Potentials vs. NHE

couple	$E°$, V vs. NHE $L \equiv$ bpy	 $L \equiv$ dmb
CoL_3^{2+}/CoL_3^+	-0.95^a	-1.07^a
CoL_2^{2+}/CoL_2^+	-1.09	-1.17
CoL^{2+}/CoL^+	-1.23	-1.29
Co^{2+}/Co^+	$\leqslant -1.6$	

^{a} Reference 12.

Table VIII. Stability Constants of bpy and dmb Complexes

	$\log K_1$	$\log K_2$	$\log K_3$
$Co(bpy)_n^{+\,a}$	$\geqslant 12^b$	7.6	6.9
$Co(dmb)_n^{+\,a}$		8.0	7.0
$Ni(bpy)_n^{2+\,c}$	7.1	6.9	6.2

^{a} At 0.2 M ionic strength. ^{b} See ref 23. ^{c} Reference 17, 0.1 M ionic strength.

the metal-bound $L^-\cdot$ chromophore.[26] The spectra of the CoL_2^+ complexes lack the intense UV bands found for CoL^+ and strongly resemble the CoL_3^+ spectra. Thus the CoL_2^+ species are considered to be Co(I) complexes.

Reduction Potentials. The reduction potentials for $Co(bpy)_3^{2+}/Co(bpy)_3^+$ and $Co(dmb)_3^{2+}/Co(dmb)_3^+$ have been measured in acetonitrile solution.[27] These may be combined with equilibrium constants for reactions 9–14 of Table IV to give the reduction potentials for all the complexes; for instance

$$E°(Co(bpy)_2^{2+}/Co(bpy)_2^+) = E°(Co(bpy)_3^{2+}/Co(bpy)_3^+) - 0.059 \log K_{11}$$

The reduction potentials calculated in this manner are given in Table VII. The $CoL_n^{2+/+}$ potentials thus range from −0.9 to −1.3 V and are more positive than those (−1.6 to −2 V) reported for macrocycle complexes,[28a] but more negative than those recently reported for oxime complexes (~−0.5 V vs. SCE in acetonitrile).[28b] As is generally found, the dmb complexes are ~0.1 V more difficult to reduce than the corresponding bpy complexes. The $E°$ values for the $CoL^{2+/+}$ couples are to be compared to those for other $M(L)/M(L^-\cdot)$ couples.[26] For $Co^{II}(bpy)/Co^{II}(bpy^-\cdot)$ the reduction potential 1–1.23 V is quite similar to that for other divalent metal centers (e.g., for $M^{II}L_3^{2+}/M^{II}L_2(L^-\cdot)^+$ (M = Fe, Ru, Os) couples, $E° \sim -1.25$ V). Only an upper limit of $E°$ for the Co^{2+}/Co^+ couple, −1.6 V, can be calculated. On the basis of this value, $K_{12} \geq 10^5$.

Stability Constants. The equilibrium constants K_9–K_{14} are also the ratios of the corresponding stability constants for the species; for example

$$\log K(Co(bpy)_3^+) - \log K(Co(bpy)_3^{2+}) = \log K_{11}$$

and the stability constants of the Co(I) complexes, based on those for the Co(II) complexes given in Table I, are given in Table VIII where stability constants of the isoelectronic nickel(II)–bipyridine complexes are summarized for comparison. It is seen directly from the magnitudes of K_{10}, K_{11} and K_{13}, K_{14} (n = 2, 3) that the stability constants for the Co(I) species are factors of 100–1500 larger than those for the corresponding Co(II) species. These results are consistent with the metal–ligand distances measured by EXAFS[29] and X-ray diffraction,[14] which indicate that the Co–N distance is 2.09 Å in $Co(bpy)_3^+$, actually 0.02 Å shorter than in $Co(bpy)_3^{2+}$, whereas metal–ligand distances in lower oxidation states are usually longer than in higher states. The small change in the bond distance between the two oxidation states has been attributed[14,29] to the fact that the extra electron in Co(I) is in a πd orbital, which increases the π bonding with the ligand to offset the effect of lower charge on Co(I). The results are also in accord with trends found for bipyridine and phenanthroline complexes of other metals: When reduction of ML_3^{3+} to ML_3^{2+} (or ML_3^{2+} to ML_3^+) involves addition of an electron to a πd orbital, K_{II}/K_{III} (or K_I/K_{II}) is greater than 1. The magnitude of the relative stabilization of the lower oxidation state varies enormously[30]—for example, for L = bpy, K_{II}/K_{III} (averaged over the stepwise stability constants) is 25, 32, and 10^6 for Cr, Fe, and Ru, respectively.[31] The relative stabilization found for $Co(bpy)_n^+$ over $Co(bpy)_n^{2+}$ ($K_I/K_{II} = 10^2$) is thus fairly large for a first-transition-series metal center. By contrast, for couples in which the electron is added to a σd orbital ($Co(bpy)_3^{3+/2+}$, $Rh(bpy)_3^{3+/2+}$, $Cu(terpy)^{2+/+}$), bpy(terpy) binding by the higher oxidation state is relatively more favorable by 10^2–10^4 depending upon the metal. The latter trend undoubtedly reflects the greater ability of the higher oxidation state to exploit the σ-donor ability of the aromatic amine. However, it is evident that $Co(I)[(\pi d)^6(\sigma d)^2]$ in the present examples resembles low-spin d^6 metal centers (such as Fe(II) and Ru(II)) in its ability to act as a π donor to bpy and related ligands. In such systems, back-bonding interactions overshadow the σ-bonding effects that must also be operative.

The Co(I) stepwise stability constants (n = 2 or 3) are about 5 times larger than those of the isoelectronic Ni(II) complexes, also given in Table VII. The metal–nitrogen distance in $Ni(bpy)_3^{2+}$ is 2.09 Å,[32,33] virtually the same as in $Co(bpy)_3^+$. The greater stability of the Co(I)– than the Ni(II)–bipyridine complexes indicates a higher relative affinity of Ni(II) for water (the values in Table VII actually reflect the relative affinities of the metal ion for L and H_2O). The inference to be drawn is that increased charge on the complex has much less effect on the stability of complexes with π-bonding ligands than it has on the stability of aquo complexes. Finally, it is noteworthy that the stability constant for $Co(bpy)^+$ is a factor of about 10^4 larger than expected from comparison with the other Ni(II) constants.[23] This is consistent with the formulation of $Co(bpy)^+$ as $Co^{II}(bpy^-\cdot)^+$ rather than as a $Co^I(bpy)^+$ species. Since the affinity of $L^-\cdot$ for H^+ (to give $LH_2^+\cdot$) is enhanced by ~10^{25} over that of L,[1b] the enhanced affinity of $L^-\cdot$ for Co(II) (a factor of 10^8 compared to that of L) is reasonable (but nonetheless striking).

Reactivities of the Co(I) Complexes. Reactions 9–14, in which the initially formed CoL_n^+ reacts with CoL_{n+1}^{2+} to give CoL_{n+1}^+ and CoL_n^{2+}, involve electron transfer: as described above, k_{obsd} varies with $[CoL_{n+1}^{2+}]$, and a substitutional process (CoL_n^+ + L) can also be ruled out because the concentration of free L is so small (e.g., if eq 9 were attributed to Co^+ + bpy, the second-order rate constant calculated would exceed 10^{11} M^{-1} s^{-1} etc). Moreover, these reactions almost certainly involve outer-sphere electron transfer. Inner-sphere equilibration pathways would be either water bridged, which would be very slow, or bpy bridged. The latter would require reaction of CoL_n^+ with that portion of

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(29) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T. K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.

(30) For a discussion of such factors, see: Van Gall, H. L. M.; Van der Linden, J. G. M. *Coord. Chem. Rev.* **1982**, *47*, 41.

(31) From the $E°$ values for the $M(H_2O)_6^{3+/2+}$ and $M(bpy)_3^{3+/2+}$ couples ($E°_{aq}$ and $E°_{bpy}$, respectively, $\log (K_{II}/K_{III}) = 16.9\,(E°_{bpy} - E°_{aq})/3$.

(32) Wada, A.; Sakabe, N.; Tanaka, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 1121.

(33) Wada, A.; Katayama, C.; Tanaka, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 3194.

CoL_{n+1}^{2+} that has a monodentate ligand. This fraction is probably less than 1%, so the rate constant calculated on the basis of total CoL_{n+1}^{+} concentration could be at most 0.01 of the diffusion-limited rate, or 10^8 M^{-1} s^{-1}, which is more than 1 order of magnitude smaller than the observed values. We therefore consider eq 9–14 in terms of a semiclassical formalism[34] appropriate to outer-sphere electron-transfer reactions and apply the Marcus cross-relation,[35] $k_{ij} = (k_{ii}k_{jj}K_{ij})^{1/2}$, to the rate constants for these reactions. Here, k_{ij} is the activation-controlled electron-transfer rate constant, k_{ii} and k_{jj} are the corresponding self-exchange rate constants for the reaction pairs, and K_{ij} is the equilibrium constant. For reactions, 10, 11, 13, and 14, the k_{ij}'s are greater than 2 × 10^9 M^{-1} s^{-1} and the K_{ij}'s are 50–200, so the various $(k_{ii}k_{jj})^{1/2}$ are greater than 2 × 10^8 M^{-1} s^{-1}. The self-exchange rate constants for the $CoL^{2+/+}$, $CoL_2^{2+/+}$, and $CoL_3^{2+/+}$ couples are thus greater than 2 × 10^8 M^{-1} s^{-1}. The rate constants for eq 9 and 12 are appreciably slower, 1 × 10^9 M^{-1} s^{-1}, while the K_{ij}'s are larger. The slowness would appear to be due to a smaller self-exchange rate constant for $Co_{aq}^{2+/+}$, less than 10^4 M^{-1} s^{-1}.

A high self-exchange rate for the $CoL_3^{2+/+}$ couples is corroborated by the results of earlier work:[1b] a self-exchange rate constant of >1 × 10^8 M^{-1} s^{-1} was estimated from the rate constants for the $LH\cdot/CoL_3^{2+}$ and LH^+/CoL_3^{+} reactions. As discussed elsewhere[14] such a higher rate is to be expected in view of the fact that the Co(II)–N and Co(I)–N bond lengths are virtually identical in $Co(bpy)_3^{2+}$ and $Co(bpy)_3^{+}$ (negligible inner-shell barrier)[14,29] and in view of the large sizes of the complex ions (small outer-shell barrier). Remarkably, the high reactivity of the $CoL_3^{2+/+}$ couples is shared by the $CoL_2^{2+/+}$ and $CoL^{2+/+}$ couples, requiring that the structural changes (between Co(II) and Co(I) and Co^{II}–L and Co^{II}–$L^-\cdot$, respectively) and resolvation that determine the barrier to electron transfer be very small for these couples as well. Thus, the Co–N and other bond lengths in CoL^{2+} and CoL^{+} and in CoL_2^{2+} and CoL_2^{+} must also be nearly identical. Finally, the high self-exchange rate for the $Co^{II}L^{2+}/Co^{II}(L^-\cdot)^+$ couples is consistent with the behavior[1b,26] of other $L/L^-\cdot$ couples such as $LH^+/LH\cdot$ and $Ru^{II}L_3^{2+}/Ru^{II}L_2(L^-\cdot)^+$.

In a discussion of the reactivity of the Co(I) species considered here, a remark about substitution reactions is warranted. Although the Co(I) substitution equilibria are maintained under pulse-radiolysis conditions by the excess and labile Co(II) species, others' observations indicate that $Co(bpy)_3^{+}$ may undergo substitution quite rapidly. In acetonitrile solvent, pseudo-first-order rate constants for replacement of bpy by acrylonitrile (equilibrium constant 1.1, rate constant 8 × 10^3 M^{-1} s^{-1} at 25 °C) exceed 10 s^{-1} with no indication of rate saturation at the highest acrylonitrile concentration.[36] If these results can be extrapolated to water solvent, the rate constant for bpy loss from $Co(bpy)_3^{+}$ is likely ≥10 s^{-1}, which is more rapid than the analogous process for $Co(bpy)_3^{2+}$. An upper limit for the rate of bpy loss is obtained by considering the reverse process, association of bpy with $Co(bpy)_2^{+}$; this reaction must have a rate constant ≤3 × 10^9 M^{-1} s^{-1}. Since the stability constant of $Co(bpy)_3^{+}$ is 8 × 10^6 M^{-1}, the rate constant for bpy loss must therefore be less than 300 s^{-1}.

Radical Reactions. The reactions of both 2-propanol radical and formate radical with the CoL_n^{2+} complexes lead to electron-transfer (Co(I)) and/or addition (CoL_nR^{2+} or $CoL_nCO_2^{+}$) products. (See Table VI.) Venturi et al. studied the reactions of 2-propanol and other alcohol radicals with phen and bpy complexes ML_3^{z+} (M = Co(III), Rh(III), Ru(II), Co(III))[24] and also found both addition and reduction reactions, depending upon the radical–ML_3^{z+} combination used. For these tris complexes as for CoL_3^{2+}, R· addition to the metal center is unlikely because no coordination sites are available for R· binding. For CoL_2^{+} and CoL_2^{2+}, coordination sites could be available but the similarities of the transient spectra and the addition rate constants to those found with CoL_3^{2+} strongly suggest that R· addition to L predominates over addition to Co(II). The $CO_2^-\cdot$ reactions have not received as extensive study as the 2-propanol reactions, but again the similarity of the rate constants for CoL_3^{2+} and CoL_n^{2+} (n = 1 or 2) is consistent with predominant ring addition.[37] Thus, in all these systems, parallel addition (eq 27) and outer-sphere

$$\mathrm{Rad}\cdot + ML_n^{z+} \xrightarrow{k_{ad}} (ML_n\mathrm{Rad})^{z+} \tag{27}$$

$$\mathrm{Rad}\cdot + ML_n^{z+} \xrightarrow{k_{el}} ML_n^{(z-1)+} + \text{product} \tag{28}$$

electron-transfer (eq 28)[22b] paths appear to operate. (Of course, it is also possible that when electron-transfer products result, they are formed in an inner-sphere process via decay of a radical adduct; i.e., $(ML_n\mathrm{Rad})^{z+}$ is an intermediate that dissociates to electron-transfer products as shown in eq 29.)

$$\mathrm{Rad}\cdot + ML_n^{z+} \rightarrow (ML_n\mathrm{Rad})^{z+} \rightarrow ML_n^{(z-1)+} + \text{product} \tag{29}$$

Both 2-propanol and formate are frequently used as scavengers in radiolytic experiments, and the resulting R· and $CO_2^-\cdot$ radicals are known to be very strong (and widely useful) reductants. The majority of the reactions of R· or $CO_2^-\cdot$ with characterized outer-sphere oxidants are very rapid, with rate constants near the diffusion-controlled limit. The reactions of the CoL_n^{2+} complexes (Table VI) with these radicals are, however, slower (because of the poor oxidizing power of Co(II)), and the activation-controlled rate constants for outer-sphere electron transfer (eq 28) provide a means of estimating the intrinsic reactivities of these radical couples. To do so, we apply the Marcus cross-relation to the rate constants for Co(I) production in eq 17, 22, 23 and 26 (i.e., for eq 22 the outer-sphere rate constant is 0.3 × (1.6 × 10^7) M^{-1} s^{-1} etc.). In order to obtain the equilibrium constants for the outer-sphere paths, K_{ij} is calculated from recent estimates of the $R^+/R\cdot$ and $CO_2/CO_2^-\cdot$ reduction potentials (−1.1[38a,b] and −1.9[38a,c] V (eq 30 and 31), respectively) and from the $CoL_n^{2+/+}$ reduction

$$(CH_3)_2COH^+ + e^- = (CH_3)_2\dot{C}OH \tag{30}$$

$$CO_2 + e^- = CO_2^-\cdot \tag{31}$$

potentials in Table VII. The Co(II)–Co(I) self-exchange rates for the $Co(bpy)_2^{2+/+}$, $Co(bpy)_3^{2+/+}$, and $Co(dmb)_3^{2+/+}$ couples are ≥1 × 10^8 M^{-1} s^{-1} as discussed above. In this manner, the $(CH_3)_2COH^{+/0}$ self-exchange rate constant is estimated as 10^5 M^{-1} s^{-1} and the $CO_2^{0/-}$ self-exchange rate constant as 10^{-5} M^{-1} s^{-1}. Although the absolute exchange rate estimates are not very reliable because of uncertainties in the reduction potentials used, it is apparent that the outer-sphere electron-transfer barrier is not large for the 2-propanol radical couple and very large indeed for the $CO_2/CO_2^-\cdot$ couple. For the former, the electron-transfer barrier is probably predominantly due to resolvation requirements. However, for the latter, extremely large inner-shell rearrangements also attend the electron transfer between linear CO_2 and bent (O–C–O angle 133°[39]) CO_2^-.[40] This structural change undoubtedly contributes to the large overpotential associated with electroreduction of CO_2 and is thus of considerable relevance in the context of ongoing efforts to catalyze CO_2 reduction.

Conclusion

The reduction of cobalt(II)–bipyridine or -dimethylbipyridine CoL_n^{2+} complexes by hydrated electrons yields the corresponding violet or blue cobalt(I) complexes for n = 2 or 3, but the bound ligand-radical complex $Co^{II}(L^-\cdot)$ for n = 1. Although the dis-

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tribution of reduced complexes (CoL_n^+ (n = 0–3)) initially produced is kinetically determined, equilibration of Co(I) and L does occur via a sequence of outer-sphere electron-transfer processes culminating in net binding of L (the equilibrium $CoL_n^+ + CoL_{n+1}^{2+} \rightleftharpoons CoL_n^{2+} + CoL_{n+1}^+$ lies to the right). The high rate constants found for these equilibrations require outer-sphere self-exchange rates greater than 10^8 M^{-1} s^{-1} for the $CoL_n^{2+/+}$ couples ($n > 0$), indicating very similar structures for CoL^{2+} and CoL^+ and for CoL_2^{2+} and CoL_2^+, as has been previously noted for CoL_3^{2+} and CoL_3^+. The stepwise binding constants for Co^+ and L are large 10^6–10^{12} M^{-1}), and the $CoL_n^{2+/+}$ reduction potentials vary from <–1.6 V (n = 0) to –0.95 V (bpy (n = 3)). The magnitudes of the stability constants of the cobalt(I) complexes and of the self-exchange rates of the Co(I)–Co(II) couples suggest the importance of Co(I) πd to $L\pi^*$ back-bonding in the CoL_2^+ and CoL_3^+ series.

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Registry No. $Co(bpy)^{2+}$, 15878-93-0; $Co(bpy)_2^{2+}$, 15878-94-1; $Co(bpy)_3^{2+}$, 15878-95-2; $Co(dmb)^{2+}$, 93503-94-7; $Co(dmb)_2^{2+}$, 93503-95-8; $Co(dmb)_3^{2+}$, 47837-98-9; $Co(bpy)^+$, 93503-96-9; $Co(bpy)_3^+$, 47780-35-8; $Co(bpy)_2^+$, 23852-07-5; $Co(dmb)^+$, 93503-97-0; $Co(dmb)_2^+$, 93503-98-1; $Co(dmb)_3^+$, 47837-97-8; $Co(bpy)R^{2+}$, 93503-99-2; $Co(bpy)_2R^{2+}$, 93530-03-1; $Co(bpy)_3R^{2+}$, 93504-00-8; $Co(dmb)R^{2+}$, 93504-01-9; $Co(dmb)_2R^{2+}$, 93504-02-0; $Co(dmb)_3R^{2+}$, 93504-03-1; $Co(bpy)CO_2^+$, 93504-04-2; $Co(bpy)_2CO_2^+$, 93504-05-3; $Co(bpy)_3CO_2^+$, 93504-06-4; $Co(dmb)CO_2^+$, 93504-07-5; $Co(dmb)_2CO_2^+$, 93504-08-6; $Co(dmb)_3CO_2^+$, 93504-09-7; R·, 5131-95-3; CO_2^-·, 14485-07-5; OH, 3352-57-6.

Contribution from the Chemistry Department,
N.R.C. Democritos, Aghia Paraskevi, Athens, Greece

Photocatalytic Generation of Hydrogen by 1:12 Heteropolytungstates with Concomitant Oxidation of Organic Compounds

A. IOANNIDIS[1] and E. PAPACONSTANTINOU*

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1:12 heteropolytungstates with the Keggin structures $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $FeW_{12}O_{40}^{5-}$ and $H_2W_{12}O_{40}^{6-}$ undergo multielectron photoreduction in the presence of a great variety of organic reagents in near-visible and UV light. Photoaddition of electrons drives the redox potential to more negative values sufficient to reduce, from a thermodynamic point of view, hydrogen ions in the presence of a Pt catalyst. It turns out that hydrogen is produced in the presence and absence of Pt. Photoreduction proceeds to the extent that the rate of photoreduction matches the back-reoxidation by H^+. The reduction step at which this takes place depends on the tungstate used. Thus, for instance, with PW_{12}^{3-} this happens at a higher reduction step than $H_2W_{12}^{6-}$, which is reduced at more negative reduction potentials. When Pt catalyst is present, the reduction potential at which the steady-state H_2 evolution is obtained is less negative. Average rate constants, from all four tungstates, of H_2 evolution at the steady state were (5.6 ± 3.1) × 10^{-4} and (2.6 ± 1.8) × 10^{-4} s^{-1} with and without Pt, respectively. The efficiency of H_2 production is of the order of one molecule of hydrogen per 100 photons absorbed. The low yield represents the low efficiency of photoproduction of higher reduction products. For $PW_{12}O_{40}^{3-}$ the quantum yields of photoaddition of the first and second electron are ca. 0.15 and 0.01, respectively.

Introduction

Heteropolycompounds (HPC) of molybdenum and tungsten are known to undergo multielectron reduction in distinct reduction steps by chemical and electrochemical means.[2] The reduction is reversible in the sense that reduced HPC can be reoxidized without decomposition. Reduction has been subsequently obtained by radiolysis through a variety of short-lived organic radicals,[3] whereas recently the multielectron photoreduction of these compounds in the presence of a variety of organic reagents has been demonstrated.[4]

It has been pointed out that reduced HPC could, from a thermodynamic point of view, reduce H^+.[5] While this work was in progress, hydrogen was produced from photoreduced $SiW_{12}O_{40}^{4-}$,[6] whereas the feasibility of hydrogen production by the chemically reduced form of this compound has been demonstrated by Russian workers,[7] who recently extended their work to photochemistry.

Table I. UV Spectral Data for Oxidized 1:12 Tungstates and Half-Wave Potentials for the First Two 1-Electron Reductions[2a]

anion	λ,[a] nm	$E_{1/2}$,[b] V	pH dependence
PW_{12}^{3-}	265.0	–0.023	none
		–0.266	none
SiW_{12}^{4-}	262.0	–0.187	none
		–0.445	none
FeW_{12}^{6-}	264.0	–0.349	none
		–0.577	below pH 4.0
$H_2W_{12}^{6-}$	257.5	–0.581	below pH 4.9
		–0.730	below pH 5.4

[a] In 1 M sulfuric acid. [b] In 1 M sulfate at 25 °C.

This paper describes and compares the photochemical production of hydrogen by a series of 1:12 tungstates in which there is a progressive variation of charge and reduction potential.

Experimental Section

The 1:12 tungstates, namely $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, $FeW_{12}O_{40}^{5-}$, and $H_2W_{12}O_{40}^{6-}$, designated for simplicity as PW_{12}^{3-}, SiW_{12}^{4-}, FeW_{12}^{5-}, and

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