Coordination Chemistry Reviews, 64 (1985) 321—341
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHOTOGENERATION AND REACTIONS OF COBALT(I) COMPLEXES

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ABSTRACT

Cobalt(I) polypyridine complexes (which are capable of reducing H^+ to H_2 and CO_2 to CO) may be generated from polypyridineruthenium(II) excited-state reactions by a variety of routes. The relation between the energetics and the rate constants for these routes are considered. In addition, factors leading to loss of cobalt(I) and the mechanisms of substrate reduction are discussed.

INTRODUCTION

In recent years polypyridineruthenium(II) complexes (RuL_3^{2+}) have attracted great interest because of their photophysical and photochemical properties and because of their ability to mediate a number of photoconversion processes (ref. 1-9). Photoreduction of water to H_2 has received particular attention, with both heterogeneous and homogeneous catalysis of H_2 formation having been achieved. Recently, RuL_3^{2+}-mediated photoreduction of CO_2 (or HCO_3^-) to CO has been effected as well (ref. 10) and systems based on cobalt(II) polypyridine catalysts operating in conjunction with RuL_3^{2+} mediators that are capable of the homogeneous photoreduction of both H_2O and CO_2 have been developed (ref. 5,7,10(a),10(b)). In these systems, cobalt(I) complexes (generated by one-electron reduction of cobalt(II)) react with the substrates H^+ (or H_2O) and CO_2 (or HCO_3^-) to effect their two-electron reduction to H_2 and CO, respectively, thus providing homogeneous catalytic routes in the photoreduction sequence. In this paper the rates and mechanisms of reduction of cobalt(II) to cobalt(I) (and loss of Co(I)) in multicomponent systems are discussed as a function of the redox properties of the reactants and the mechanisms for reaction of the cobalt(I) with H^+ and HCO_3^- are considered.

0010-8545/85/$07.35

EXCITED-STATE REACTION PATHWAYS

The polypyridineruthenium(II) metal-to-ligand charge-transfer excited states ($*RuL_3^{2+}$) are relatively long lived and may undergo bimolecular reactions with electron acceptors ("oxidative quenching", eq. 2), electron donors ("reductive quenching", eq. 3), or energy acceptors (energy transfer, eq. 4) where L = 2,2'-bipyridine or 1,10-phenanthroline, A is an electron acceptor, D is an electron donor, and *En is the excited state of energy acceptor En (refs. 1-4). Upon excitation of RuL_3^{2+} (eq. 1), a metal-centered

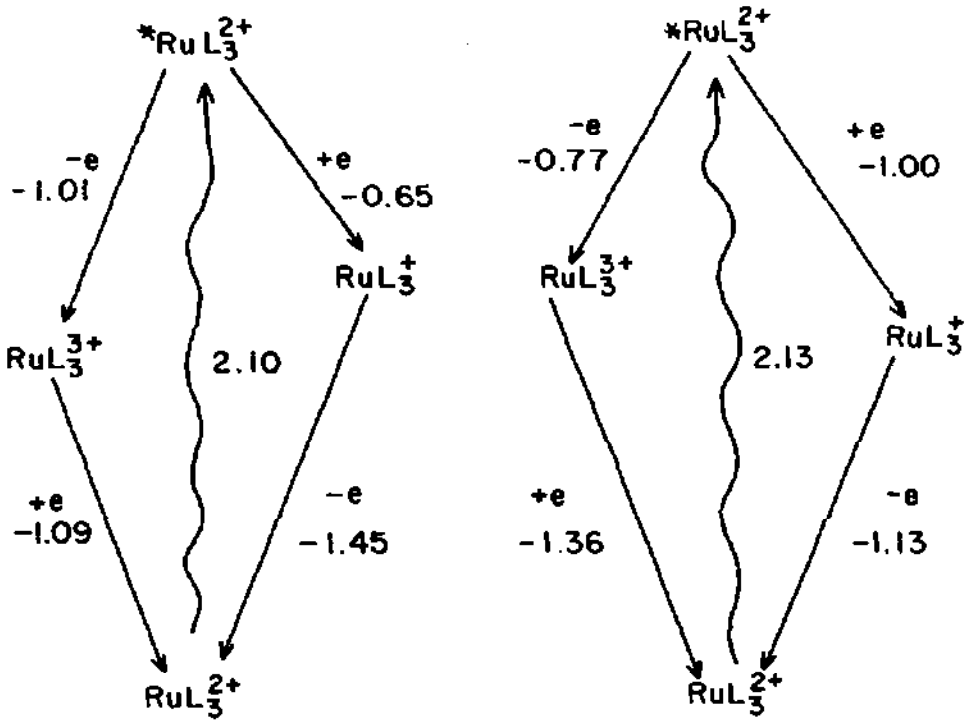
$$RuL_3^{2+} \underset{\text{heat; } 1/k \sim 1\ \mu s}{\overset{h\nu;\ \lambda \leqslant 550\ \text{nm}}{\rightleftharpoons}} *RuL_3^{2+} \qquad (1)$$

$$*RuL_3^{2+} + A \longrightarrow RuL_3^{3+} + A^- \qquad (2)$$

$$*RuL_3^{2+} + D \longrightarrow RuL_3^{+} + D^+ \qquad (3)$$

$$*RuL_3^{2+} + En \longrightarrow RuL_3^{2+} + *En \qquad (4)$$

4d electron is promoted to a ligand-centered (polypyridine π^*) orbital and strongly oxidizing (Ru^{3+}) and reducing (L^-) sites are thereby created. As the excitation energy of the excited state is ~ 2 eV, both electron donor and acceptor properties of the complex are strongly enhanced over those of the ground state. This is shown below for two different complexes.



L= 4,7-$(CH_3)_2$ phen L= 5 Cl-phen

Fig. 1. Free-energy diagram for RuL_3^{2+}. Data from ref. 1,6.

The rates of (outer-sphere) electron transfer from or to $*RuL_3{}^{2+}$ (eq. 2,3) are a function of the self-exchange rates and E^0's (Table 1) of the relevant couples. The rates of energy transfer from $*RuL_3{}^{2+}$ to En are a function of $RuL_3{}^{2+}$ - En spectral overlap, with the overlap between the En absorption spectrum and $RuL_3{}^{2+}$ emission spectrum (λ_{max} 605-630 nm) determining the energetics of the energy transfer.

SELF EXCHANGE

Oxidative Quenching (eq. 2)

$*RuL_3{}^{2+} + RuL_3{}^{3+} \longrightarrow RuL_3{}^{3+} + *RuL_3{}^{2+}$ $\quad k \sim 6 \times 10^8\ M^{-1}\ s^{-1}$

$A + A^- \longrightarrow A^- + A$ $\quad k_{A,A^-}$

Reductive Quenching (eq. 3)

$*RuL_3{}^{2+} + RuL_3{}^{+} \longrightarrow RuL_3{}^{+} + *RuL_3{}^{2+}$ $\quad k \sim 1 \times 10^8\ M^{-1}\ s^{-1}$

$D + D^+ \longrightarrow D^+ + D$ $\quad k_{D,D^+}$

TABLE 1

Reduction potentials vs NHE for $RuL_3{}^{3+}/*RuL_3{}^{2+}$, $*RuL_3{}^{2+}/RuL_3{}^{+}$, $RuL_3{}^{3+}/RuL_3{}^{2+}$ and $RuL_3{}^{2+}/RuL_3{}^{+}$ couples (ref. 1,5,6)

L	$*E^0_{3,2}$, V	$*E^0_{2,1}$, V	$E^0_{3,2}$, V	$E^0_{2,1}$, V
bpy	-0.84	+0.84	+1.26	-1.28
4,4'-$(CH_3)_2$bpy	-0.94	+0.69	+1.10	-1.37
5-Clphen	-0.77	+1.00	+1.36	-1.15
phen	-0.87	+0.79	+1.16	-1.36
5-(CH_3)phen	-0.90	+0.89	+1.23	-1.31
4,7-$(CH_3)_2$phen	-1.01	+0.67	+1.09	-1.47

Because the spectral properties of $RuL_3{}^{2+}$ do not change significantly with L, but the redox properties do, a useful approach (ref. 6) to determining the nature of the $RuL_3{}^{2+}$ quenching mechanism has been to ascertain how the quenching rate constant k_q changes with the properties of $*RuL_3{}^{2+}$. Data illustrating this approach are presented in Fig. 2. With Eu^{3+}, ($E^\circ_{3,2}$ = -0.4 V) the rate constants increase as the reducing power of $*RuL_3{}^{2+}$ increases (i.e. as E^0 for the $RuL_3{}^{3+}/*RuL_3{}^{2+}$ couple becomes more negative) as expected for excited-state oxidation (eq. 2, A = Eu^{3+}). This conclusion has been confirmed by identifying the products $RuL_3{}^{3+}$ and Eu^{2+}_{aq} spectrally in flash-photolysis experiments (ref. 6). With ascorbate ion, the opposite rate trend is observed: quenching rate constants diminish as $*E^\circ_{3,2}$ becomes more negative but increase with $*E^\circ_{2,1}$ -- that is as the oxidizing power of $*RuL_3{}^{2+}$ increases (ref. 7). Reaction according to eq. 3 (D = HAs^-) is thus

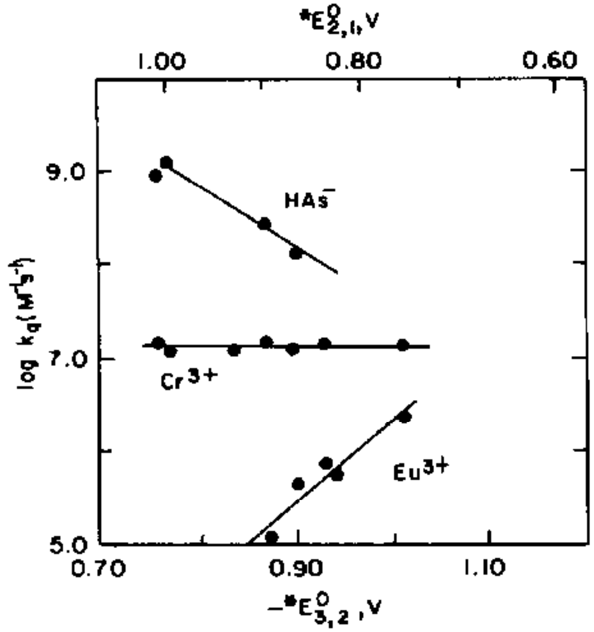


Fig. 2. Plot of the logarithm of the quenching rate constant versus the reduction potential for (bottom) the $RuL_3^{3+}/*RuL_3^{2+}$ and (top) the $*RuL_3^{2+}/RuL_3^{+}$ couple for various phen and bpy derivatives. Data are from ref. 7, 6, and 6 for ascorbate ion (HAs^-), $Cr(H_2O)_6^{3+}$, and Eu_{aq}^{3+}, respectively.

implicated and again has been confirmed (ref. 8) by spectral detection of RuL_3^{+}. By contrast, with $Cr(H_2O)_6^{3+}$, k_q is insensitive to the nature of RuL_3^{2+}, consistent with energy transfer (eq. 4) producing ground state RuL_3^{2+} and a ligand-field excited state of $Cr(H_2O)_6^{3+}$.

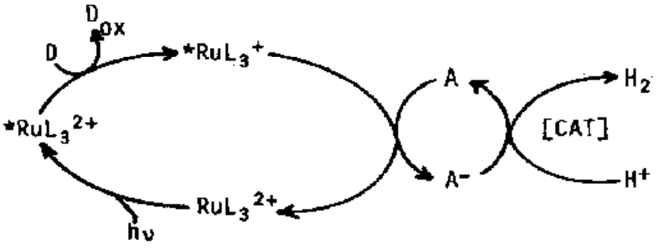
PHOTOREDUCTION PATHWAYS

Rather remarkably, in the multicomponent systems used to carry out net photochemistry (e.g. photoreduction of CO_2 or H_2O) any of the three quenching routes may eventually lead to the same net products. Oxidative and reductive quenching routes to the net change

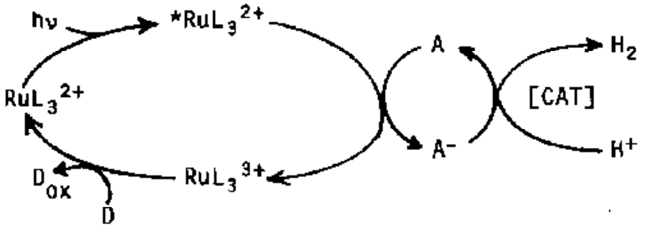
$$h\nu + D + H^+ \xrightarrow{RuL_3^{2+},\ A} D_{ox} + 1/2\ H_2$$

are illustrated below where "CAT" may be an added heterogeneous catalyst (e.g. Pt) (refs. 5,7,9,10).

I. Reductive Quenching



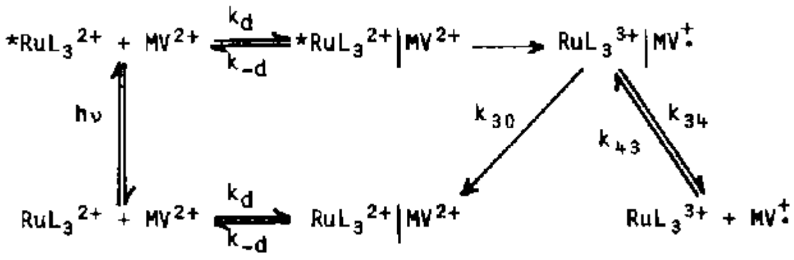
II. Oxidative Quenching



[If the primary energy-transfer products RuL_3^{2+} and *En undergo subsequent electron transfer to produce RuL_3^+ and En^+ or RuL_3^{3+} and En^-, then the same schemes apply (I or II with $D_{ox} = En_{ox}$ or $A^- = En^-$, respectively).] Which route obtains depends upon the redox properties of RuL_3^{2+}, A, and D (and, in some cases, upon their concentrations). For example with A = methyl viologen (MV^{2+}) and D = triethanolamine (TEOA), H_2 is photo-generated in the presence of colloidal platinum via the oxidative route when L = bpy (ref. 3) but via the reductive route if L = bipyrazine (ref. 11). Thus the net chemistry observed does not necessarily provide information about the mechanism.

Which of the above routes is most effective in producing the desired product (here, H_2) is determined by the efficiencies of several steps which may differ greatly for the various routes. A common feature is the separation of the quenching products (cage escape). As is shown in Scheme III for MV^{2+} quenching of $*RuL_3^{2+}$, diffusion apart of the newly formed RuL_3^{3+} and $MV^{\dot{+}}$

III. Cage Escape



$$MV^{\dot{+}} + H^+ \xrightarrow{[Pt]} MV^{2+} + 1/2\ H_2$$

occurs in competition with (extremely exergonic) "back" electron transfer to form ground-state RuL_3^{2+} and MV^{2+}. The yield of separated species (~ 0.1 in water at 25 °C; ref. 9, 12), is determined by the ratio $\phi_{cage} = k_{34}/(k_{30} + k_{34})$. In subsequent steps RuL_3^{3+} is reduced to RuL_3^{2+} and the $MV^{\dot{+}}$ undergoes catalyzed reaction with H^+. In suitable systems, the latter two steps may be effected with 100% chemical efficiency so that the overall quantum yield for H_2 production is determined by ϕ_{cage}. Consequently, the

H_2 yield is, in principle, much higher with the reductive route (TEOA donor, $Ru(bpz)_3^{2+}$) because the yield of separated $TEOA^{\dot{+}}$ and $Ru(bpz)_3^{+}$ (which rapidly reduces MV^{2+} to $MV^{\dot{+}}$) is ~ 0.5 (ref. 11, 12). Although the cage-escape yield is universally limiting (in bimolecular systems) and is relevant to all the systems considered in this paper, other additional reactions (for example, $TEOA^{\dot{+}}$ oxidation of $MV^{\dot{+}}$ in competition with $MV^{\dot{+}}$ reduction of water) may lower product yields and determine which RuL_3^{2+}, D, A combination is most effective for a given purpose.

POLYPYRIDINE COBALT(II) SYSTEMS

The original strategy adopted in seeking homogeneous catalysts for RuL_3^{2+} mediated water reduction was to couple the one-electron changes associated with the RuL_3^{2+} couples to the two-electron changes for H^+ reduction through a labile metal center with three suitable oxidation states (ref. 1a,13,14). Because of their redox properties and reactivities, a number of cobalt(II) complexes offered promise as potential catalysts. Reduction potentials for polypyridine cobalt couples are presented in Table 2.

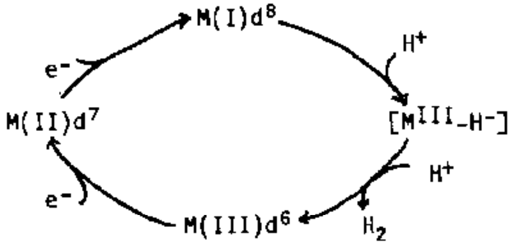


TABLE 2
Reduction potentials for $CoL_3^{3+/2+}$, $CoL_3^{2+/+}$, and $CoL_3^{3+/+}$ couples vs NHE (ref. 5)

L	$E^0_{3,2}$, V	$E^0_{2,1}$, V	$E^0_{3,1}$, V
bpy	+0.30	-0.95	-0.33
$(CH_3)_2$bpy	+0.16	-1.07	-0.45
5-Clphen	+0.50	-0.83	-0.18
phen	+0.37	-0.93	-0.29
4,7-$(CH_3)_2$phen	+0.19	-1.07	-0.44
terpy[a]	+0.26	-0.76	-0.25

[a] For $Co(terpy)_2^{n+}$ (ref. 15).

From the values in Tables 1 and 2 it is evident that CoL_3^{2+} can be reduced to CoL_3^{+} by either $^*RuL_3^{2+}$ or RuL_3^{+}. Furthermore, from the $E^{\circ}_{3,1}$ values in Table 2, Co(I) complexes are strong enough reductants to reduce H^+ (or CO_2) to H_2 (or CO) in a two-electron reaction (see Fig. 1 in ref. 10a).

Since Co(III) is reduced by Co(I), the net reaction is given by eq. 6 for which ΔG° is ~ -0.5 eV at pH 7, 1 atm H_2.

$$Co(I) + H^+ \longrightarrow Co(II) + 1/2\ H_2 \qquad (6)$$

At present, several photoreduction systems employing CoL_3^{2+} complexes have been characterized: cases in which Co(II) is produced through reaction with RuL_3^+ (ref. 7, 14) (Scheme II, D = HAs^-) and with $*RuL_3^{2+}$ (ref. 5) (Scheme I, D = TEOA) are known. Factors operating in the latter type of system in which Co(II) is the quencher will be considered next.

Quenching Mechanisms

The interaction of CoL_3^{2+} with $*RuL_3^{2+}$ is potentially especially complicated because both reactants can act as either electron donor or acceptor (see Tables 1 and 2). Thus either (or both) eq. 2 or 3 may occur in addition to energy transfer (eq. 4). In one system based on $*Ru(4,7-(CH_3)_2phen)_3^{2+}$ and $Co(bpy)_3^{2+}$, the products Ru(III) and Co(I) are found to form with a quantum yield of 0.3 in 50 % aq. acetonitrile (ref. 5) -- suggesting an oxidative quenching mechanism. However, in contrast to the behavior found for Eu^{3+} in Fig. 2, with $Co(bpy)_3^{2+}$ k_q values do not vary significantly with the reduction potential of the RuL_3^{2+} excited state used. In fact, for all the RuL_3^{2+} and CoL_3^{2+} combinations studied, k_q varies only from ~0.6×10^9 to ~1.2×10^9 $M^{-1}\ s^{-1}$ in aqueous media and is definitely below the diffusion-controlled value (~3×10^9 $M^{-1}\ s^{-1}$) expected for reactants of this type under these conditions. In addition, there are excellent reasons to expect contributions from parallel reductive and energy-transfer quenching pathways. Consequently the redox and spectral characteristics of the ruthenium(II) and cobalt(II) polypyridine complexes will be considered in some detail using $Co(bpy)_3^{2+}$ as an example.

Energy transfer to cobalt(II). As noted earlier, RuL_3^{2+} complexes emit in the visible with λ_{max} = 605-630 nm. All "octahedral" cobalt(II) complexes exhibit ligand-field transitions in this region. In Figure 3, overlap of the $Co(bpy)_3^{2+}$ absorption spectrum and the $Ru(bpy)_3^{2+}$ emission spectrum are compared. Evidently the $Ru(bpy)_3^{2+}$ emission overlaps both the 11.3 kK (quartet-quartet) and 16.0 kK (quartet-doublet) $Co(bpy)_3^{2+}$ absorption bands reasonably well. Thus the energetic criteria for energy transfer from $*Ru(bpy)_3^{2+}$ to $Co(bpy)_3^{2+}$ are met [although the electronic factor for the process cannot be predicted with any confidence (ref. 2(a))].

Electron-transfer quenching by cobalt(II) complexes. Notwithstanding the production of RuL_3^{3+} and $Co(bpy)_3^+$ in the L = $4,7-(CH_3)_2phen$ system, $Co(bpy)_3^{2+}$ can also reduce the RuL_3^{2+} excited states. Reduction potentials

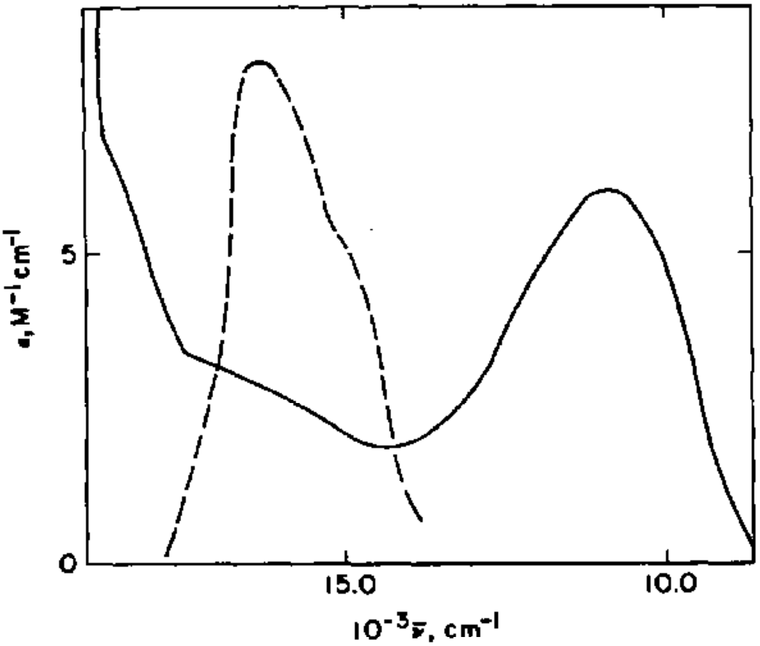


Fig. 3. Overlap of $Ru(bpy)_3^{2+}$ emission spectrum (dashed line, arbitrary scale) and $Co(bpy)_3^{2+}$ absorption spectrum (solid line) in aqueous solutions at 25 °C.

for both Co(III)-Co(II) and Co(II)-Co(I) couples were given in Table 2. Both $E^\circ_{3,2}$ and the $E^\circ_{2,1}$ values follow trends established for other metal centers: the E^0's become more negative as the free ligand pK_a increases. This is shown in Fig. 4 where data for RuL_3 couples are also plotted. From the $E^\circ_{3,2}$ data for cobalt in Table 2 and the $^*E^\circ_{2,1}$ values in Table 1 it is evident that reductive quenching (eq. 3) is thermodynamically favorable for any of the cobalt(II)-$^*RuL_3^{2+}$ combinations. The driving force for oxidative quenching (eq. 2) is smaller and actually thermodynamically unfavorable in a number of cases. Remarkably, because of the linear free-energy relations shown in Figure 4, as the driving force for reductive quenching increases, that for oxidative quenching diminishes in a linear fashion. This is illustrated for $Co(bpy)_3^{2+}$ with different RuL_3^{2+} excited states in Fig. 5.

Although the thermodynamic considerations indicate that reductive quenching should predominate with CoL_3^{2+}, kinetic factors operate which diminish this thermodynamic advantage. The intrinsic electron-transfer barriers for Co(III)-Co(II) couples are much greater than those for Co(II)-Co(I) couples. This is illustrated by the self-exchange rate constants for $Co(bpy)_3^{n+}$ at 0.1 M ionic strength:

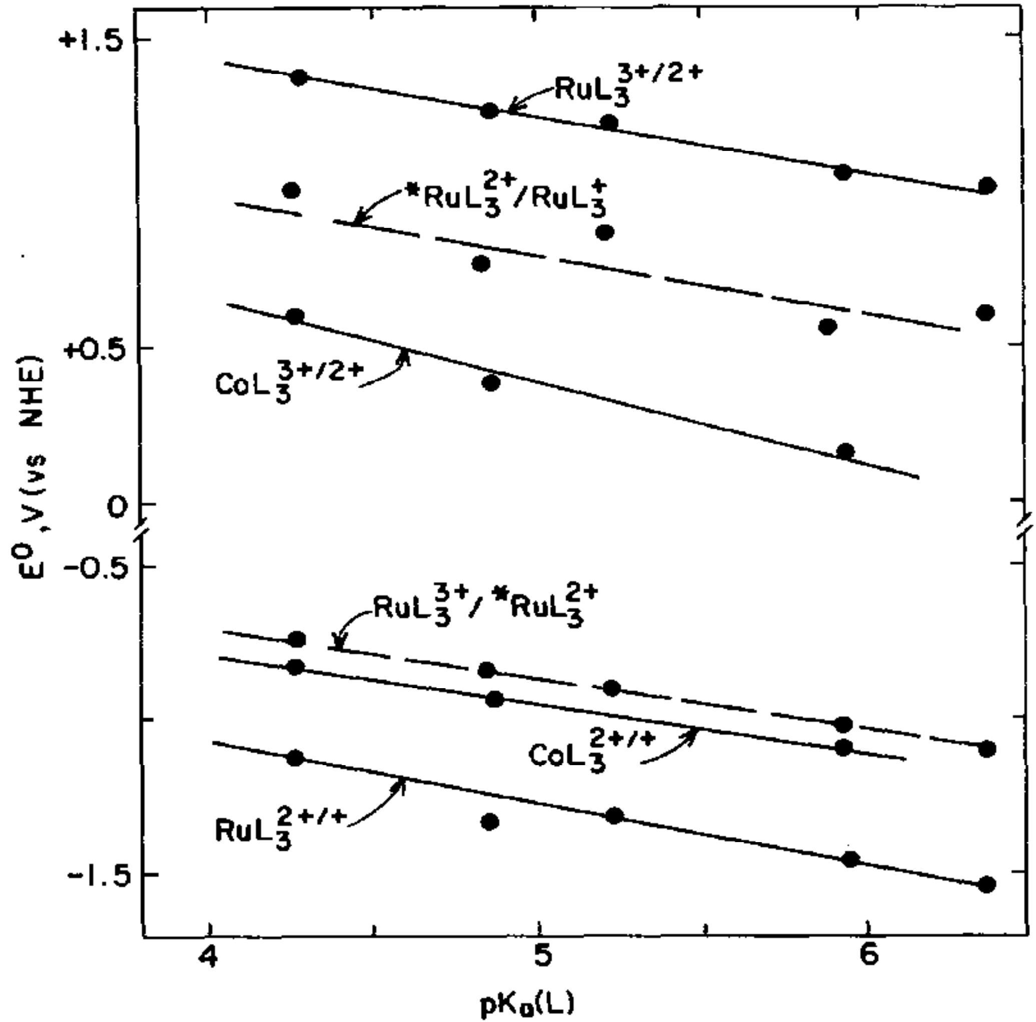


Fig. 4. Reduction Potentials of ML_3 couples versus ligand pK_a values.

SELF EXCHANGE (ref. 16)

$Co(bpy)_3^{2+} + Co(bpy)_3^{3+} \rightarrow Co(bpy)_3^{3+} + Co(bpy)_3^{2+}$ $k = 18\ M^{-1}\ s^{-1}$

$Co(bpy)_3^{+} + Co(bpy)_3^{2+} \rightarrow Co(bpy)_3^{2+} + Co(bpy)_3^{+}$ $k = 6 \times 10^8\ M^{-1}\ s^{-1}$

Thus since reduction of $Co(bpy)_3^{2+}$ to $Co(bpy)_3^{+}$ is favored by an intrinsic kinetic factor of ~ 5 x 10^3 (the square root of the self-exchange rates) the oxidation processes should become competitive only when the equilibrium constant for oxidation is ~ 3 x 10^7 greater than for reduction (free-energy difference ~0.4 eV). From the data in Fig. 5 the free-energy differences for oxidation and reduction of $Co(bpy)_3^{2+}$ range from -0.3 to -0.7 eV, suggesting that, depending on the RuL_3^{2+} used, either reductive or oxidative processes, or both, may play a significant role, along with the energy-transfer path discussed above.

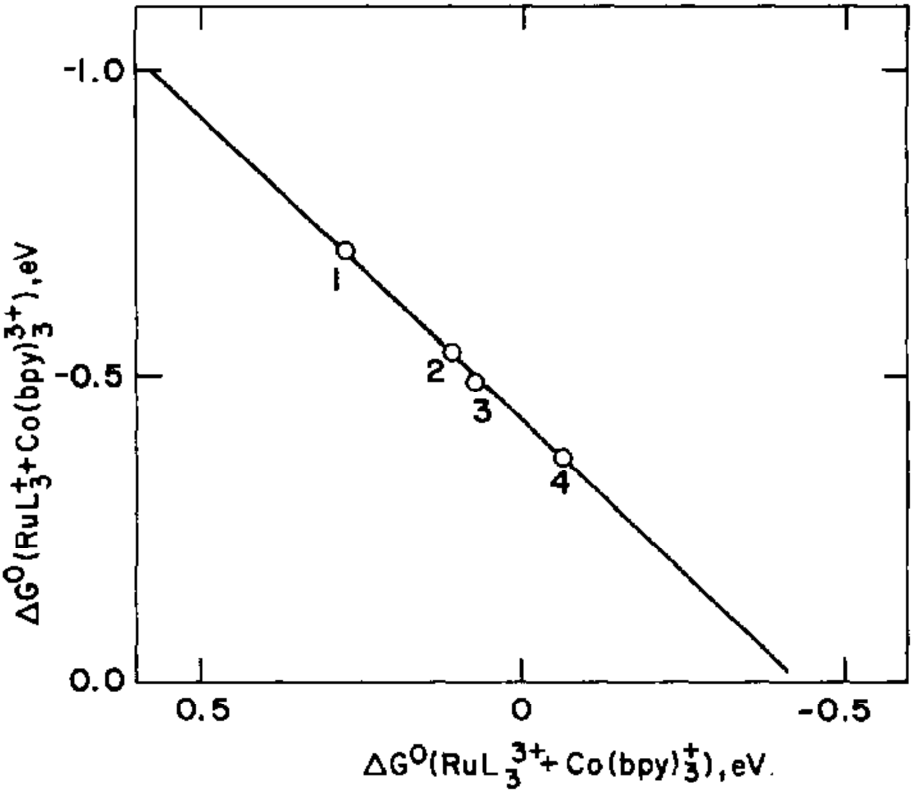
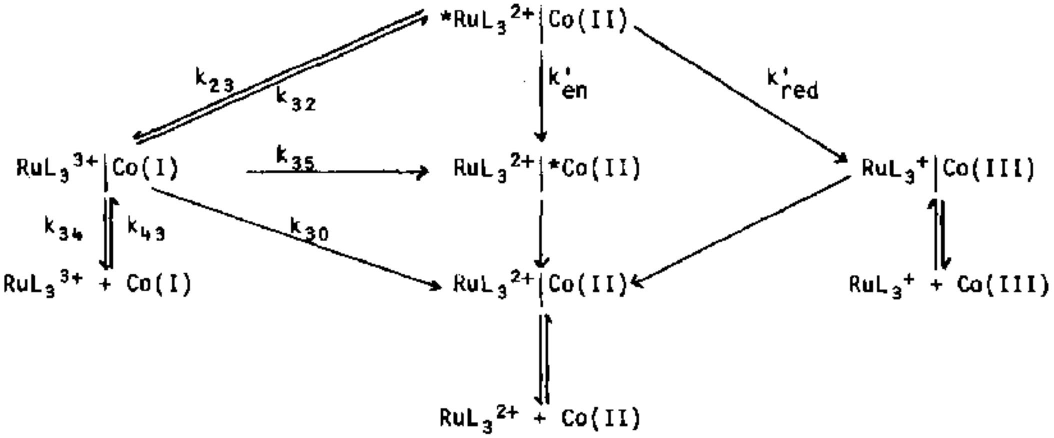


Fig. 5. Free-energy changes for $*RuL_3^{2+}$ - $Co(bpy)_3^{2+}$ reactions. ΔG^0 for production of RuL_3^+ and $Co(bpy)_3^{3+}$ (eq. 3) vs. ΔG^0 for production of RuL_3^{3+} and $Co(bpy)_3^+$ (eq. 2).

Parallel quenching pathways. Because the three reaction pathways (eq. 2-4) may occur through one pair of reactants, the three paths must be treated simultaneously. This is done in the following scheme:

$$*RuL_3^{2+} + Co(II) \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} *RuL_3^{2+}|Co(II)$$



which gives the following expression for k_q when the steady-state approximation is applied to the concentrations of the various intermediates:

$k_q = k_{red} + k_{ox} + k_{en}$, where

$k_{red} = [k_d\, k'_{red}\, (k'_{30} + k'_{32} + k_{34})]/\mathrm{DEN}$,

$k_{ox} = [k_d\, k_{23}\, (k'_{30} + k_{34})]/\mathrm{DEN}$,

$k_{en} = [k_d\, k'_{en}\, (k'_{30} + k_{32} + k_{34})]/\mathrm{DEN}$,

$\mathrm{DEN} = (k_{-d} + k_{23} + k'_{red} + k'_{en})(k'_{30} + k_{34}) + k_{32}(k_{-d} + k'_{red} + k'_{en})$

and $k'_{30} = (k_{30} + k_{35})$.

The values of k_{red}, k_{ox}, k_{en}, and k_q calculated from the above equations for $Co(bpy)_3{}^{2+}$ quenching of $*RuL_3{}^{2+}$ are plotted vs the driving force for oxidative quenching in Fig. 6. The points are $Co(bpy)_3{}^{2+}$ quenching rate constants at μ = 0.5 M (ref. 5).

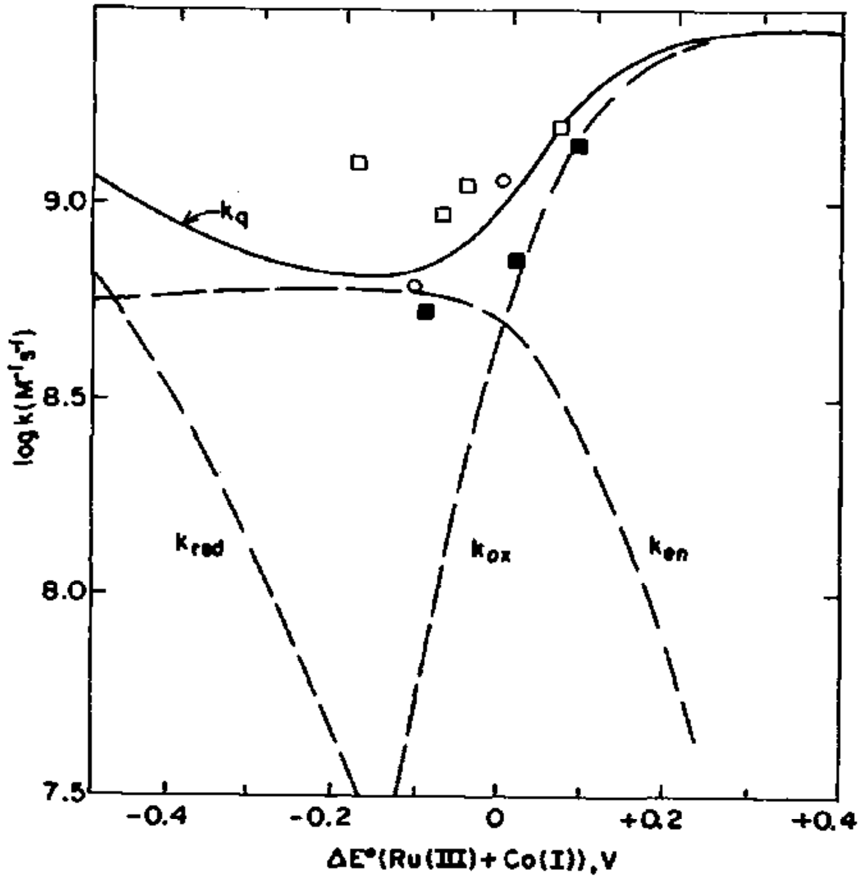


Fig. 6. Values of k_{red}, k_{ox}, k_{en} and k_q for quenching of $*RuL_3{}^{2+}$ emission by $Co(bpy)_3{}^{2+}$ as a function of the driving force for production of Co(I) and Ru(III). For details see ref. 5.

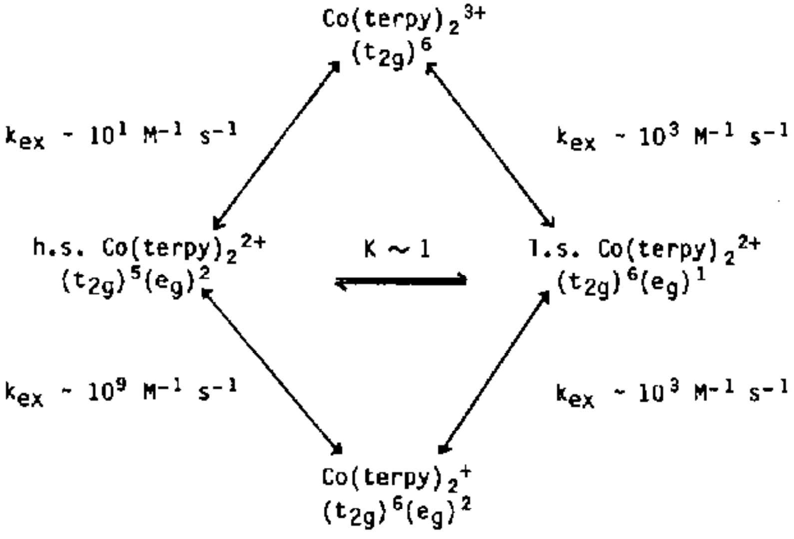
Several aspects of the plots in Fig. 6 merit comment. The first is the negligible ($\leq$ 10%) contribution of the highly thermodynamically favorable reductive pathway to the net quenching rate constant. As discussed above, the small magnitude of k_{red} is a consequence of the slow $Co(bpy)_3^{3+/2+}$ exchange rate and the poor electronic factor for the net reaction (to produce RuL_3^+ and $Co(bpy)_3^{3+}$). In sharp contrast, the magnitude of k_{ox} is quite large, even at zero driving force, and dominates the quenching process at $\Delta E^o \gtrsim 0.1$ V. This behavior is a consequence of the high $Co(bpy)_3^{2+/+}$ and $RuL_3^{3+}/{}^*RuL_3^{2+}$ self-exchange rates and the favorable electronic factor for the formation of $Co(bpy)_3^+$ and RuL_3^{3+}. Finally, in many cases there is a substantial contribution from an energy-transfer path ($k_{en} \sim$ 0.8×10^9 M^{-1} s^{-1} with $Ru(bpy)_3^{2+}$). Interestingly, although (the first-order) k_{en}' was assumed constant in calculating Fig. 6, the effective contribution of k_{en} to k_q drops when the oxidative path is favorable because of the relative rapidity of the k_{23} process. A final noteworthy aspect of the quenching is that the energetics in the present system are such that the oxidative quenching products RuL_3^{3+} + $Co(bpy)_3^+$ may undergo subsequent electron transfer (k_{3S}) to yield RuL_3^{2+} and excited $Co(bpy)_3^{2+}$--the same products produced in the energy transfer step. However, the $Co(bpy)_3^{2+}$ excited state is not a sufficiently strong (or reactive) reductant to reduce RuL_3^{2+} to RuL_3^+. Thus in this particular system energy transfer products do not give rise to electron transfer products (although the converse may be true).

In summary, for the $Co(bpy)_3^{2+}$-${}^*RuL_3^{2+}$ combination three parallel quenching processes (eq. 2-4) are energetically possible. However, because of the slow electron transfer rate associated with the Co(III)-Co(II) couple, only two of these processes, oxidative quenching and energy-transfer quenching, operate to a significant extent. Because of the low energy content (and low redox reactivity and short lifetime) of the excited $Co(bpy)_3^{2+}$, no redox products derive from its decay. With the strongly reducing ${}^*Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$ complex, quenching occurs almost exclusively via excited state oxidation and the $Co(bpy)_3^+$ observed in this system arises from the latter process.

Parallel Quenching Paths in Related Systems.

Neglecting, for the moment, the energy-transfer process, it is interesting to consider how the redox products, Co(I) and RuL_3^{3+}, or Co(III) and RuL_3^+, can be "tuned" (ref. 17) by altering substituents on the reactant complexes. One approach is to drastically alter the E^o's of either the cobalt or the ruthenium couples by sufficiently changing the ligands. For example, replacement of the bipyridine or phenanthroline ligands on Ru(II) by bipyrazine ligands thermodynamically favors formation of $Co(bpy)_3^{3+}$ and RuL_3^+ to such an extent that reductive quenching should predominate since $^*Ru(bpz)_3^{2+}$ is both a stronger oxidant and poorer reductant than $^*Ru(bpy)_3^{2+}$ by ca. 0.5 V (ref. 11). By contrast, changing to the combination $Co(bpm)_3^{2+}$ - RuL_3^{2+} markedly favors oxidative quenching (bpm = bipyrimidine; $\Delta G°$ -0.1 to -0.5 eV depending on RuL_3^{2+}) and eliminates the possibility of reductive quenching because the cobalt(II) complex is an extremely poor reductant ($E°_{3,2}$ = +1.02 V; ref. 18).

An alternative to the above strategy would be to alter the intrinsic electron-transfer barriers (exchange rates) for the cobalt couples instead of (or in addition to) introducing drastically different thermodynamics. This could, in principle, be done by using $Co(terpy)_2^{2+}$ for which high- and low-spin states are in rapid (ref. 19, 20) equilibrium (K ~ 1) in water at room temperature. For the low-spin $Co(terpy)_2^{2+}$ - $Co(terpy)_2^{3+}$ couple the exchange rate constant is ca. $10^3\ M^{-1}\ s^{-1}$, (ref. 21) and the rate constant for the high-spin $Co(terpy)_2^+$ - low-spin $Co(terpy)_2^{2+}$ exchange should be comparable. The exchange rates for the couples involving high-spin $Co(terpy)_2^{2+}$ should be similar to those for the $Co(bpy)_3$ series.



For $Co(terpy)_2^{2+}$, the energetics of oxidative and reductive quenching are similar to those for $Co(bpy)_3^{2+}$. Since with the high-spin complex the intrinsic barriers for Co(I) and Co(III) formation from Co(II) are also expected to be very similar to those for $Co(bpy)_3^{2+}$, Co(I) formation is kinetically favored over Co(II) formation. By contrast, with low-spin

$Co(terpy)_2^{2+}$ as reactant the intrinsic barriers for Co(III) and Co(I) production are comparable so that the thermodynamics (which favor Co(III) over Co(I)) should predominate, i.e.

$$\text{h.s. } Co(terpy)_2^{2+} + {}^*Ru(bpy)_3^{2+} \xrightarrow{} Co(terpy)_2^{+} + Ru(bpy)_3^{3+}$$

KINETIC CONTROL

but

$$\text{l.s. } Co(terpy)_2^{2+} + {}^*Ru(bpy)_3^{2+} \xrightarrow{} Co(terpy)_2^{3+} + Ru(bpy)_3^{+}$$

THERMODYNAMIC CONTROL

In practice, however, the behavior is likely to be complicated by contributions from energy-transfer paths and by the rates of interconversion of high- and low-spin states.

PHOTOREDUCTION SYSTEMS BASED ON Co(II) COMPLEXES

Generation of Cobalt(I)

From the above discussion it is evident that cobalt(I) can be produced by electron transfer from $^*RuL_3^{2+}$ to Co(II). Indeed with $^*Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$ and $Co(bpy)_3^{2+}$ this is the predominant (> 90%) quenching pathway and yields separated RuL_3^{3+} and $Co(bpy)_3^{+}$ with a cage-escape yield of 0.3 in 50% aq. acetonitrile (ref. 5). Excited-state quenching by cobalt(II) can give rise to Co(I) by other routes as well: For example, $RuL_3^{2+}|^*Co(II)$ (energy-transfer products) could undergo electron transfer to give $RuL_3^{3+}|Co(I)$ (but this is unlikely for the systems considered here). Finally, even when Co(III) is the quenching product (reductive quenching by Co(II)), Co(I) may be generated through secondary reactions (e.g. TEOA· or RuL_3^{+} may reduce Co(II)). Similarly, other routes to Co(I) obtain when Co(II) is not the quencher. With HAs^- is donor (Scheme I), reductive quenching of $^*Ru(bpy)_3^{2+}$ gives RuL_3^{+} with ca. 0.5 cage-escape yield (ref. 8) and RuL_3^{+} reduces Co(II) to Co(I) (ref. 7,14). In fact, even Scheme II could yield Co(I): with $^*Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, a rhodium(III) or iridium(III) polypyridine complex as acceptor, and triethanolamine as donor, RhL_3^{2+} or IrL_3^{2+} produced in the quenching could reduce Co(II) to Co(I) (with the appropriate ligands for Rh(III), Ir(III) and Co(II)). Systems of the latter type, although more complex in composition, might provide higher Co(I) yields because of higher cage-escape yields and/or because of elimination of the losses due to energy transfer that may occur when Co(II) is the quencher. Evidently, depending upon the nature of the ligands bonded to Ru(II) and Co(II) and other components in the system, a number of photochemical routes may be used to generate CoL_3^{+}. An important factor determining the relative efficiencies of the different routes is the suppression of back reactions. This is considered next.

Loss of Cobalt(I)

All photoinduced electron-transfer reactions are subject to direct back-reactions (e.g. for RuL_3^{2+} - MV^{2+} in Scheme III, bimolecular reaction of RuL_3^{3+} and $MV^{+\cdot}$ gives ground-state RuL_3^{2+} and MV^{2+} with $k_{th} = k_{43}k_{30}/k_{34}$). In sacrificial donor systems, direct back-reactions are suppressed by rapidly eliminating one primary product (e.g. RuL_3^{3+} is reduced by added EDTA or TEOA). Frequently, however, secondary loss processes are introduced as a consequence. For example (ref. 9), reduction of RuL_3^{3+} by TEOA yields RuL_3^{2+} and $TEOA^{+\cdot}$ (a strongly oxidizing nitrogen-centered radical cation). Oxidation of $MV^{+\cdot}$ by $TEOA^{+\cdot}$ occurs with nearly as great a rate constant as the primary (RuL_3^{3+} + $MV^{+\cdot}$) back-reaction which is eliminated at high [TEOA] by bimolecular $TEOA^{+\cdot}$ "rearrangement" to give $TEOA^{'\cdot}$ (a carbon-centered radical derived from TEOA by H-atom abstraction from CH_2) which is a poor oxidant and a very strong reductant.

Secondary loss reactions in CoL_3^{2+} systems are even more involved because of the potential oxidation of CoL_3^{2+} to CoL_3^{3+}: the oxidation of CoL_3^{+} by CoL_3^{3+} ($\Delta G^0 \leq -1$ eV) is extremely rapid (ref. 7), but reduction of CoL_3^{3+} by the common sacrificial donors is not. This is aptly illustrated by the $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, $Co(bpy)_3^{2+}$, TEOA (50% aq. acetonitrile) system (ref. 5). In this system, the quantum yields for H_2 formation display a complex dependence on triethanolamine and $Co(bpy)_3^{2+}$ concentrations and are actually a function of the ratio of these concentrations, as shown in Fig. 7.

The behavior in Fig. 7 signals a twofold competition between TEOA and $Co(bpy)_3^{2+}$ for the precursors leading to H_2, with TEOA promoting and $Co(bpy)_3^{2+}$ preventing H_2 formation, despite the fact that $Co(bpy)_3^{2+}$ is essential as quencher. This competition arises from the fact that $Co(bpy)_3^{2+}$ reduces both RuL_3^{3+} and $TEOA^{+\cdot}$ thereby suppressing the irreversible formation of the strongly reducing $N(CH_2\dot{C}HOH)(CH_2CH_2OH)_2$ radical $TEOA^{'\cdot}$ and introducing $Co(bpy)_3^{3+}$, an extremely effective (ref. 7) scavenger of $Co(bpy)_3^{+}$, i.e.

$$\begin{array}{llllll}
{}^{*}RuL_3^{2+} & + & Co(bpy)_3^{2+} & \longrightarrow & RuL_3^{3+} & + \; Co(bpy)_3^{+} \\
(RuL_3^{3+} & + & Co(bpy)_3^{+} & \longrightarrow & RuL_3^{2+} & + \; Co(bpy)_3^{2+}) \\
RuL_3^{3+} & + & Co(bpy)_3^{2+} & \longrightarrow & RuL_3^{2+} & + \; Co(bpy)_3^{3+} \\
RuL_3^{3+} & + & TEOA & \longrightarrow & RuL_3^{2+} & + \; TEOA^{+\cdot} \\
Co(bpy)_3^{2+} & + & TEOA^{+\cdot} & \longrightarrow & Co(bpy)_3^{3+} & + \; TEOA \\
TEOA & + & TEOA^{+\cdot} & \longrightarrow & TEOA^{'\cdot} & + \; TEOAH^{+} \\
Co(bpy)_3^{+} & + & Co(bpy)_3^{3+} & \longrightarrow & 2Co(bpy)_3^{2+} & \\
TEOA^{'\cdot} & + & Co(bpy)_3^{2+} & \longrightarrow & TEOA_{ox} & + \; Co(bpy)_3^{+} \\
Co(bpy)_3^{+} & + & H_2O & \longrightarrow & Co(bpy)_3^{2+} & + \; \frac{1}{2}H_2 \; + \; OH^{-}
\end{array}$$

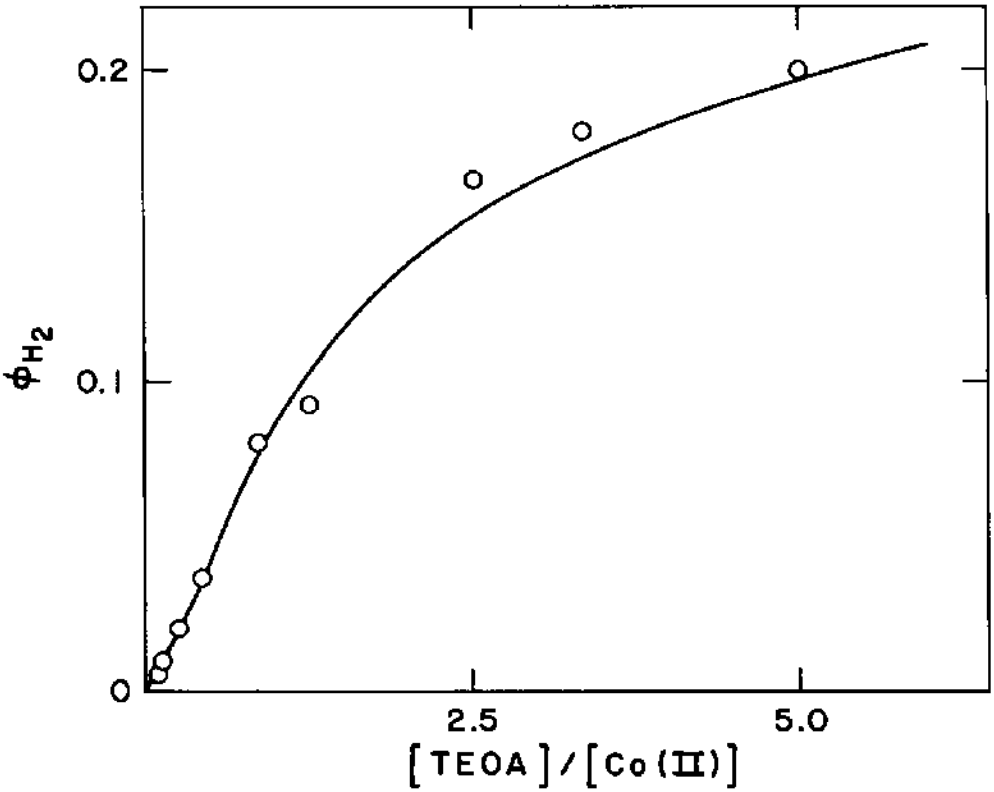


Fig. 7. Quantum yields for H_2 production as a function of the ratio of triethanolamine-to-$Co(bpy)_3^{2+}$ concentrations in 50% aq. acetonitrile with $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$ (ref. 5).

[Note that, from the above considerations, a RuL_3^{2+}, Co(II), TEOA system in which the dominant quenching yields RuL_3^+ and Co(III) (e.g. $Ru(bpz)_3^{2+}$, $Co(bpy)_3^{2+}$ at low [TEOA]) will not likely lead to high product yields: Since the reaction of TEOA with Co(III) is extremely slow, Co(III) accumulates and oxidizes $Ru(bpz)_3^+$ or Co(I) before permanent products (H_2) can be formed.]

Reactions of Cobalt(I)

To date three substrates have been found to undergo CoL_3^{2+} mediated photoreduction with RuL_3^{2+} sensitizers:

$bpy + 2H^+ + 2e \longrightarrow bpyH_2$ (ref. 7,14)
$2H^+ + 2e \longrightarrow H_2$ (ref. 7,14)
$CO_2 + 2H^+ + 2e \longrightarrow CO + H_2O$ (ref. 10a-c)

At pH 7, the two-electron reduction potentials for the substrates are -1.05, -0.41, and -0.53 V vs. NHE, respectively. In the ascorbate, $Ru(bpy)_3^{2+}$, Co(II), L (bpy or 4,4'-$(CH_3)_2$bpy)) systems at pH 3-6, H_2 and reduced ligand (LH_2) are formed (ref. 7, 14). With the aim of establishing the mechanism(s) of LH_2 and H_2 formation, extensive flash-photolysis (ref. 7) and pulse-radiolysis studies (ref. 7, 22-25) were undertaken. The latter led to the evaluation of the equilibrium constants presented in Table 3.

TABLE 3
Equilibrium constants for reactions involving polypyridine cobalt(I) complexes (ref. 22-24).

Eq.	Reaction	log K	
		bpy	dmb
(7)	$CoL_3^+ + LH^+ \rightleftharpoons CoL_3^{2+} + LH\cdot$	-1.39	-0.89
(8)	$LH\cdot + H^+ \rightleftharpoons LH_2^{\dot{+}}$	8.0	9.3
	$CoL_3^+ + LH^+ + H^+ \rightleftharpoons CoL_3^{2+} + LH_2^{\dot{+}}$	6.61	8.4
(9)	$CoL_3^+ + LH_2^{\dot{+}} \rightleftharpoons CoL_3^{2+} + LH_2$	7.29	---
(10)	$CoL_3^+ + H_3O^+ \rightleftharpoons CoL_2(H_2O)H^{2+} + L$	0	1.3[a]
(11)	$CoL_3^+ + 2H_2O \rightleftharpoons CoL_2(H_2O)_2^+ + L$	-6.9	-7.0
(12)	$CoL_2(H_2O)_2^+ + H^+ \rightleftharpoons CoL_2(H_2O)H^{2+} + H_2O$	6.9	8.3[a]
(13)	$CoL_3^+ + 2H^+ \rightleftharpoons CoL_3^{3+} + H_2$	11.3	15.3[b]
(14)	$CoL_2(H_2O)H^{2+} + H^+ + L \rightleftharpoons CoL_3^{3+} + H_2$	11.3	14[b]

[a] Ref. 25.

[b] Calculated from data in Table 2 and earlier data in this Table.

In the above ascorbate system, dihydrobipyridine formation appears to arise predominantly through one-electron reduction steps, i.e. (ref. 22)

$$Co(bpy)_3^+ + bpyH^+ \rightleftharpoons Co(bpy)_3^{2+} + bpyH\cdot \qquad k_7 = 1.8 \times 10^8\ M^{-1}\ s^{-1} \qquad (7)$$

$$bpyH\cdot + H^+ \rightleftharpoons bpyH_2^{\dot{+}} \qquad (8)$$

$$Co(bpy)_3^+ + bpyH_2^{\dot{+}} \longrightarrow Co(bpy)_3^{2+} + bpyH_2 \qquad (9)$$

Indeed dihydrobipyridine formation occurs on photolysis of bpy, $Ru(bpy)_3^{2+}$, ascorbate solutions in the absence of Co(II) (ref. 7), and, in the latter system, only one-electron outer-sphere pathways (involving the strong reductant $Ru(bpy)_3^+$) are likely. The high rate constants for eq. 7 reflect the fact that intrinsic barriers for both $Co(bpy)_3^{2+/+}$ and $bpyH^{+/0}$ couples are small. (The rate constant for eq. 9 has not been determined.)

By contrast, the formation of H_2 from the reaction of $Co(bpy)_3^+$ with H^+ or H_2O involves an intermediate hydrido complex which reacts with a proton source to give H_2. Surprisingly, the rate-determining step in the formation of the hydrido complex $CoL_2(H_2O)H^{2+}$ under pulse-radiolysis and ascorbate photolysis conditions (pH < 7; [Co(II)] > [L]) also involves the outer-sphere one-electron transfer reaction eq. 7 (ref. 22). Evidently the hydrido complex is assembled in the rapid ensuing reaction of bpyH• with Co(II) (present in quite high concentrations in the pulse-radiolysis and photolysis experiments), i.e.

$$\mathrm{Co(I)} + \mathrm{bpyH^+} \longrightarrow \mathrm{Co(II)} + \mathrm{bpyH\cdot} \quad \text{slow}$$
$$\mathrm{bpyH\cdot} + \mathrm{Co(II)} \longrightarrow\ \longrightarrow \mathrm{Co(bpy)_2(H_2O)H^{2+}} \quad \text{fast}$$

The hydrido complex then undergoes reaction with water or H^+ (k_{obsd} ~ 0.1 and 1 s^{-1} at pH 7 with L = bpy and dmb, respectively, at pH 7, 25 °C; ref. 25) to produce H_2 and Co(III); Co(III) is rapidly reduced to Co(II) (ref. 7) giving the net stoichiometry in eq. 6. A remarkable feature of these systems is that under typical pulse-radiolysis or photolysis conditions reactions 7-12 are at equilibrium on the ca. 0.1 s time scale, with the positions of the equilibria being a function of total Co(II) and L concentrations and the pH ([Co(I)] ≪ [Co(II)]). The equilibria are maintained through outer-sphere electron-transfer reactions such as

$$\mathrm{Co(bpy)_2(H_2O)_2{}^{2+}} + \mathrm{Co(bpy)_3{}^{+}} \rightleftharpoons \mathrm{Co(bpy)_2(H_2O)_2{}^{+}} + \mathrm{Co(bpy)_3{}^{2+}}$$

and eq. 7 and through rapid Co(II) substitutional equilibria, e.g.

$$\mathrm{Co(bpy)_3{}^{2+}} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Co(bpy)_2(H_2O)_2{}^{2+}} + \mathrm{bpy}$$

Interestingly, it appears that the relative yields of H_2 and LH_2 are determined to a considerable extent by the positions of these equilibria: the LH_2 yield parallels the equilibrium fraction of "cobalt(I)" present as $LH_2^{+\cdot}$ (eq. 7, 8); conversely the H_2 yield parallels the equilibrium fraction of "cobalt(I)" present as $CoL_2(H_2O)H^{2+}$ (eq. 9, ref. 25). At pH ≥ 4 the overall yield (LH_2 + H_2) drops as the pH is increased in the ascorbate system because of very rapid oxidation of CoL_3^+, the dominant form of "cobalt(I)" at high pH, by ascorbate radical.

In basic solutions, photolysis of $Ru(bpy)_3^{2+}$ or $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, $Co(bpy)_3^{2+}$, triethanolamine mixtures in mixed solvents yields H_2 (and, in the presence of CO_2, CO). In contrast to the above ascorbate systems which incur secondary back-reaction losses (HAs• + Co(I) + HAs^- + Co(II)) at high pH, the TEOA donor systems are, in principle, limited only by ϕ_{cage} at sufficiently high TEOA: in the absence of HCO_3^-, $\phi_{H_2} = \phi_{cage}$ (ref. 5). In these systems, not only is the pH much higher than in the ascorbate systems, but the [L]-to-[Co(II)] ratio is much greater as well. Thus [L] ≫ [H^+], eq. 10 lies to the left and CoL_3^+ (rather than $CoL_2(H_2O)H^{2+}$ or $LH_2^{+\cdot}$) is the dominant form of cobalt(I). In addition, the rate of $Co(bpy)_2(H_2O)H^{2+}$ formation by the one-electron processes above is very slow. The rate law obtained in conventional experiments at 10^{-4} to 10^{-3} M Co(I) (concentrations higher than those in the photochemical systems at steady state) in the presence of 5 to

10-fold excess $Co(bpy)_3{}^{2+}$ is, however, consistent with the formation of $Co(bpy)_2(H_2O)H^{2+}$ as an intermediate: the term is first-order in $[Co(bpy)_3{}^+]$ and $[H^+]$ and inverse in [bpy] (ref. 10a,26). Hydrogen is evidently produced through the reaction of $Co(bpy)_2(H_2O)H^{2+}$ with water, and, as above, Co(III) is reduced by Co(I) to give the net stoichiometry in eq. 6.

With added $HCO_3{}^-$ (ref. 10a) the rate law for $Co(bpy)_3{}^+$ reaction with $HCO_3{}^-$ is of the same form as above and first-order in $[HCO_3{}^-]$, indicating that $Co(bpy)_2(H_2O)H^+$ may react with $HCO_3{}^-$, as well as with H_2O, i.e.

$$Co(bpy)_2(H_2O)H^{2+} + HCO_3{}^-/H_2O \longrightarrow \text{Products}$$

However, because of the limited pH range studied, the kinetically equivalent reaction of $Co(bpy)_2(H_2O)_2{}^+$ and CO_2 is also possible for the $HCO_3{}^-$ reaction (ref. 10a).

It is evident that H_2 and CO production require binding of the substrates H^+ and $HCO_3{}^-$ or CO_2 to the cobalt center. Thus some comment on the substitutional steps is merited. As discussed above, in the low pH (low[L]) media studied by pulse radiolysis, substitution of Co(I) (e.g. eq 11) is effected through electron-transfer reactions amongst Co(I) and Co(II) species (ref. 24). Thus the high substitutional lability of Co(II) and the high outer-sphere electron-transfer reactivity of the Co(II)-Co(I) couples preclude rate-determining substitution on Co(I). However, as noted earlier, under the TEOA photolysis conditions the redox-catalyzed pathways for $Co(bpy)_2(H_2O)H^{2+}$ formation are not sufficiently rapid to account for the rates observed. Thus a different mechanism for generation of the hydrido complex must be operative and it very likely involves substitution on cobalt(I) e.g.

$$Co(bpy)_3{}^+ \rightleftharpoons Co(bpy)_2(H_2O)^+ + bpy \qquad \text{ligand dissociation}$$
$$Co(bpy)_2(H_2O)^+ + H^+ \rightleftharpoons Co(bpy)_2(H_2O)H^{2+} \qquad \text{proton addition}$$

Loss of bpy from $Co(bpy)_3{}^+$ in acetonitrile occurs with $k_{obsd} \geq 10\ s^{-1}$ (ref. 27). Thus high-spin cobalt(I) is a substitutionally labile metal center and the above sequence is a reasonable one. In the $HCO_3{}^-/CO_2$ reaction at least two possibilities for substrate binding must be considered: binding of CO_2 to $Co(bpy)_2(H_2O)_2{}^+$ (substitution on Co(I)), and binding of $HCO_3{}^-$ to $Co(bpy)_2(H_2O)H^{2+}$ (substitution on Co(III) labilized by the presence of coordinated H^-). At present both routes appear viable.

To conclude, the cobalt(I) complexes can react with a variety of substrates and are effective in reducing bpy to $bpyH_2$, H_2O to H_2, and CO_2 to CO. An important feature of these reactions is the substitution lability of high-spin cobalt(I) and cobalt(II) (and perhaps also cobalt(III) as the hydride). The substitution lability of the cobalt complexes contrasts with the inertness of the ruthenium complexes: while the relative inertness of the latter complexes renders them ideal electron-transfer reagents, so that bimolecular quenching reactions can successfully compete with the natural decay of the ruthenium(II) excited states, the lability of the cobalt complexes is required to effect useful chemistry. In addition, the high outer-sphere electron transfer reactivity of the $CoL_3^{2+/+}$ couples enables facile generation of Co(I) from Co(II) and the RuL_3^{2+} excited-state reactions. It is this combination of electron-transfer and substitutional reactivities which is responsible for the net catalytic sequence.

SUMMARY

Cobalt(I) polypyridine complexes can be prepared photochemically from cobalt(II) complexes using ruthenium(II) polypyridine complexes as sensitizers. Reduction of the excited ruthenium(II) complex (to form RuL_3^+ and D_{OX}), oxidation of the excited complex (to form RuL_3^{2+} and A^-) and, in principle, energy transfer (to form RuL_3^{2+} and *En) can all generate cobalt(I) under suitable conditions. Although the yield of cobalt(I) is determined by a variety of competing reactions, progress in modeling the systems is being made and the cobalt(I) yields can be predicted with some confidence. Depending upon conditions the photogenerated Co(I) complexes may be used to reduce a variety of substrates. Reduction of H^+ to H_2 and of CO_2 to CO occur through cobalt-substrate complexes. Rapid reaction is promoted by the high substitutional reactivity of Co(II), Co(I) and the hydrido cobalt(III) complex. Thus the cobalt(II) complexes catalyze photoreduction reactions by rapid outer-sphere electron-transfer reactions yielding cobalt(I) and rapid bond-making and breaking reactions yielding products (e.g. H_2 or CO) and regenerating cobalt(II).

ACKNOWLEDGMENTS

We gratefully acknowledge the work of our collaborators C. V. Krishnan and H. A. Schwarz who have made invaluable contributions to our understanding of the cobalt systems. This research was carried out at Brookhaven National Laboratory which is operated under contract DE-AC-02-76-CH00016 with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences.

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