**Table III.** Volumes of Activation for Complex Formation Reactions of $Co^{2+}$ and $Ni^{+}$ with Neutral Ligands in Aqueous Solution

| entering ligand | $\Delta V^{*}$, $cm^3 mol^{-1}$ | | ref |
|---|---|---|---|
| | $Co^{2+}$ | $Ni^{2+}$ | |
| $H_2O$ | +6.1 ± 0.2 | +7.2 ± 0.3 | 12 |
| bpy | +4.3 ± 1.0 | +5.5 ± 0.3 | this work[a] |
| | +7.5 ± 1.4 | +5.1 ± 0.4 | this work[b] |
| terpy | +4.5 ± 0.8 | +6.7 ± 0.2 | this work[a] |
| | +3.7 ± 1.3 | +4.5 ± 0.4 | this work[b] |
| $NH_3$ | +4.8 ± 0.7 | +6.0 ± 0.3 | 26 |
| pada[c] | +7.2 ± 0.2 | +7.7 ± 0.3 | 26 |
| | +11.2 ± 2.5 | +8.2 ± 2.1 | 30 |
| | +5.3 ± 0.5 | | 43 |
| imidazole | | +11.0 ± 1.6 | 29 |
| isoquinoline | | +7.4 ± 1.3 | 44 |

[a] Determined from the data for [L] >> [M] in Table II. [b] Determined from the data for [M] >> [L] in Table II. [c] pada = pyridine-2-azo-(*p*-dimethylaniline).

from $I_a$ to $I_d$ for $Mn^{2+}$ and $Fe^{2+}$, respectively.[3-14,31] Unfortunately the extreme pH sensitivity of the $Fe^{2+}$–bpy system prevented further studies of this system, and we are presently in search of suitable alternatives.

The activation volumes for the complex formation reactions of $Co^{2+}$ and $Ni^{2+}$ with bpy and terpy fit well into the range of values summarized for various complex formation reactions of these ions in Table III. No effort is made to compare these data with those for systems involving charged entering ligands,[27,28,44-48] since significant corrections of the measured $\Delta V^{*}$ for ion-pair formation is required in such cases. These corrections are usually based on theoretical predictions[49,50] and cause some uncertainties with respect to the resulting $\Delta V^{*}$ values. The results in Table III underline the validity of the $I_d$ mechanism for such ligand-exchange processes involving $Co^{2+}$ and $Ni^{2+}$.

To summarize, the present study has shown that the earlier suggested changeover in the solvent-exchange mechanism for the first-row transition-metal elements also applies to complex formation reactions involving these metal ions and neutral ligands. Two complete sets of volume of activation data for complex formation of $Mn^{2+}$, $Fe^{2+}$, $Co^{2+}$, and $Ni^{2+}$ with bpy and terpy are now available, and these underline the mechanistic discrimination ability of this activation parameter. We therefore cannot go along with general statements casting doubt on the value of volumes of activation in mechanistic investigations.[51] Plausible theoretical explanations for the observed mechanistic changeover along the first-row transition-metal elements have been given elsewhere.[14]

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**Registry No.** bpy, 366-18-7; terpy, 1148-79-4; Mn, 7439-96-5; Fe, 7439-89-6; Co, 7440-48-4; Ni, 7440-02-0.

**Supplementary Material Available:** Tables A and B including all averaged $k_{obsd}$ values as a function of [M], [L], and pressure (7 pages). Ordering information is given on any current masthead page.

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# Kinetics of Reduction of Cobalt(III) Complexes by Viologen Radicals

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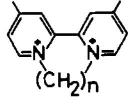
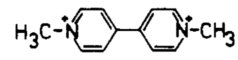
The second-order rate constants are reported for reduction of 11 cobalt(III) complexes by viologen radicals, derived from diquaternary salts of 4,4′-bipyridine and 2,2′-bipyridine. Rate constants vary from $1.5 \times 10^2$ to $6.0 \times 10^8$ $M^{-1} s^{-1}$, and an excellent correlation with the Marcus expression for 14 redox reactions is observed. These data conform, on the basis of a unity transmission coefficient, to a self-exchange rate constant for the viologens ($X^{2+/+}$ couple) of $1.5 \times 10^6$ $M^{-1} s^{-1}$. It is suggested however that this value is about $10^2$ too low.

Diquaternary salts of 2,2′-bipyridine, 4,4′-bipyridine, and 1,10-phenanthroline form very interesting radicals by one-electron reduction.[1,2] Most studied have been those from diquat (1,1′-ethylene-2,2′-bipyridylium ion, **1a**) and (particularly) paraquat



1a, $n = 2$, R = H ($DQ^{2+}$)
b, $n = 2$, R = $CH_3$ ($MDQ^{2+}$)
c, $n = 3$, R = H ($PDQ^{2+}$)
d, $n = 4$, R = H ($BDQ^{2+}$)

(1,1′-dimethyl-4,4′-bipyridylium ion, **2**), which are employed as



**2** ($MV^{2+}$)

herbicides[3] and used as mediators of one-electron-transfer processes in, for example, solar energy conversion and storage.[4,5] No systematic study of the kinetics of reduction of metal complexes by these types of radicals has been reported. We have chosen as oxidants a variety of cobalt(III) complexes with neutral ligands (hence all are +3 charged). These have been well characterized with respect to both reduction potentials and self-exchange rate constants, and this is important for use in Marcus-type calculations. The five viologen radicals chosen can be easily prepared from the viologens (**1**, **2**) by dithionite reduction, and the radicals are relatively stable in anaerobic media.[6] Some kinetic data on $MV^{+\cdot}$ reduction of $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$ have been reported previously.[7,8]

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## Experimental Section

Cobalt(III) complexes were prepared by standard literature methods. $Co(sep)^{2+}$ was generated in situ by Zn/Hg reduction of $Co(sep)^{3+}$.[9] $Co(diNOsar)(ClO_4)_3$ was prepared by a slight variation[10] of a recipe originating in Dr. Sargeson's laboratory and recently published.[11] $(PDQ)Br_2{\cdot}H_2O$, $(BDQ)Br_2{\cdot}H_2O{\cdot}{}^1/_3HBr$, and $(MDQ)Br_2{\cdot}H_2O$ were prepared as described in the literature.[12] The remaining chemicals used were the purest commercial products. All complexes and viologens had the expected spectral characteristics. The radicals were prepared by adding 0.95 equiv of $S_2O_4^{2-}$ to the oxidized viologen and in some experiments by irradiating 30–60 μM oxidized viologen ($MV^{2+}$, $DQ^{2+}$, or $PDQ^{2+}$), 0.1–5 mM EDTA, and 5 μM 3,10-dimethyl-5-deazaisoalloxazine with light from a 500-W bulb for 30–60 s.[13] The concentration of viologen radical was assessed spectrally by using the following absorbance coefficients, $M^{-1}\ cm^{-1}$ (see ref 6): $\epsilon_{760} = 2.7 \times 10^3$ ($DQ^{+}\cdot$); $\epsilon_{600} = 1.3 \times 10^4$ ($MV^{+}\cdot$); $\epsilon_{760} = 2.9 \times 10^3$ ($MDQ^{+}\cdot$); $\epsilon_{493} = 2.0 \times 10^3$ ($PDQ^{+}\cdot$); $\epsilon_{500} = 2.5 \times 10^3$ ($BDQ^{+}\cdot$).

**Kinetics.** Carefully deaerated solutions of cobalt(III) complex (0.5–20 mM) and reduced viologen (25–100 μM) in the appropriate buffer (0.1 M Tris/$H_2SO_4$) at the proper ionic strength (0.5 M $Na_2SO_4$) were mixed in a Gibson-Dionex stopped-flow apparatus interfaced with an OLIS data-collecting system. The reactions were followed by the loss of radical in the 470–500-nm region (and at other wavelengths with similar results). In general, excellent first-order rates were observed. For pulse-radiolysis experiments, mixtures of Co(III) complexes and $MV^{2+}$ (each 0.3–2.0 mM) at pH 7.6, $I$ = 0.03 M with a phosphate buffer, and 5% *t*-BuOH) in deaerated solution were electron pulsed (~4 μM $e_{aq}^-$). A quartz cell with a 2.4-cm path length was used. Excellent first-order loss of $MV^{+}\cdot$ (at 600 nm) by reaction with the Co(III) complexes was observed. For the experiments in acid perchlorate, $MV^{+}\cdot$ formed photochemically in $Na_2SO_4$ solutions (0.1 mM EDTA and 5 μM 3,10-dimethyl-5-deazaisoalloxazine) was mixed with perchloric acid and/or sodium perchlorate in the stopped-flow apparatus.

## Results

All the radicals examined were sufficiently stable at neutral pH in a sulfate medium[6] so that their reactions with cobalt(III) complexes could be studied. Reactions of $MV^{+}\cdot$ with several cobalt(III) complexes in different conditions were investigated. In neutral solution the radical was stable in ionic strengths as high as 2.0 M provided the medium was $Na_2SO_4$, but $MV^{+}\cdot$ decomposed in a few minutes when 1 M $NaClO_4$ was used. A sulfate medium was always used therefore for the generation of $MV^{+}\cdot$ for all experiments. The radical generated in neutral solution by dithionite reduction of $MV^{2+}$ was very unstable when transferred to an acid medium. That however produced by the photochemical method had sufficient stability as follows: in 0.05 M $HClO_4$ ($I$ = 0.1 M with $Na_2SO_4$), 5–10 μM $MV^{+}\cdot$ decomposed with $t_{1/2} \sim 0.6$–1.0 s; in 1 M $HClO_4$ ($I$ = 2.0 M with $Na_2SO_4$), $t_{1/2} \sim 0.3$–0.5 s. The decay of the radical was quite a good second-order process ($2k \sim 2 \times 10^6\ M^{-1}\ s^{-1}$). Sufficient cobalt(III) complex was used so that all the reactions studied were much faster than the decay of $MV^{+}\cdot$ radical.

Complete oxidation of the viologen radicals by the cobalt(III) complexes was observed. This would be anticipated from the values of the reduction potentials of the reacting species. Plots of $k_{obsd}$, the pseudo-first-order rate constant, vs. [cobalt(III) complex], in excess, were linear with zero intercepts. The slope of the plot gave $k_1$, the second-order rate constant for reaction of the radical $X^{+}\cdot$

$$Co(III) + X^{+}\cdot \rightarrow Co(II) + X^{2+} \quad k_1 \qquad (1)$$

**Table I.** Rate Constants for Reduction of Cobalt(III) Complexes by Pyridyl Radicals at 25 °C, $I$ = 0.5 M (with $Na_2SO_4$)

| reactants | $k_1$, $M^{-1}\ s^{-1}$ |
|---|---|
| $Co(en)_3^{3+}$–$DQ^{+}\cdot$ | $(1.5 \pm 0.1) \times 10^{2\,a}$ |
| $Co(en)_3^{3+}$–$MV^{+}\cdot$ | $(1.3 \pm 0.1) \times 10^{3\,a}$ |
| $Co(en)_3^{3+}$–$MDQ^{+}\cdot$ | $(1.3 \pm 0.1) \times 10^{3\,a}$ |
| $Co(en)_3^{3+}$–$PDQ^{+}\cdot$ | $(2.5 \pm 0.2) \times 10^{3\,b}$ |
| $Co(en)_3^{3+}$–$BDQ^{+}\cdot$ | $(1.2 \pm 0.1) \times 10^{3\,c}$ |
| $Co(chxn)_3^{3+}$–$DQ^{+}\cdot$ | $47 \pm 3^{a}$ |
| $Co(NH_3)_6^{3+}$–$DQ^{+}\cdot$ | $(5.0 \pm 0.5) \times 10^{3\,a}$ |
| $Co(NH_3)_5py^{3+}$–$DQ^{+}\cdot$ | $(3.3 \pm 0.2) \times 10^{4\,b}$ |
| $Co(NH_3)_5py^{3+}$–$MV^{+}\cdot$ | $(1.9 \pm 0.3) \times 10^{5\,b}$ |
| $Co(sep)^{3+\,d}$–$DQ^{+}\cdot$ | $(1.2 \pm 0.1) \times 10^{4\,b}$ |
| $Co(sep)^{3+}$–$MV^{+}\cdot$ | $(7.0 \pm 0.3) \times 10^{4\,a,c}$ |
| $Co(sep)^{3+}$–$MDQ^{+}\cdot$ | $(1.0 \pm 0.04) \times 10^{5\,b}$ |
| $Co(sep)^{3+}$–$BDQ^{+}\cdot$ | $(1.1 \pm 0.1) \times 10^{4\,c}$ |
| $Co(diNOsar)^{3+\,e}$–$DQ^{+}\cdot$ | $(9.3 \pm 0.5) \times 10^{5\,b}$ |
| $Co(diNOsar)^{3+}$–$MDQ^{+}\cdot$ | $(5.8 \pm 0.4) \times 10^{6\,b}$ |
| $Co(diNOsar)^{3+}$–$Co(sep)^{2+}$ | $(8 \pm 2) \times 10^{2\,b}$ |
| $Co(edta)^{-}$–$DQ^{+}\cdot$ | $(1.3 \pm 0.2) \times 10^{7\,a}$ |
| $Co(ox)_3^{3-}$–$DQ^{+}\cdot$ | $>3 \times 10^{7\,a}$ |
| $Co(phen)_3^{3+}$–$MV^{+}\cdot$ | $(1.1 \pm 0.3) \times 10^{8\,f}$ |
| $Co(terpy)_2^{3+}$–$MV^{+}\cdot$ | $5.8 \times 10^{8\,f}$ |
| $Co(bpy)_3^{3+}$–$MV^{+}\cdot$ | $(6.0 \pm 0.6) \times 10^{8\,f}$ |

[a] pH 7.2. [b] pH 7.8. [c] pH 9.2. [d] sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.[19] [e] diNOsar = 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane.[19] [f] pH 7.6, $I$ = 0.03 M with phosphate buffer.

**Table II.** Effect of $H^+$ and $ClO_4^-$ Ions on the Reduction of Cobalt(III) Complexes by Methylviologen Radicals at 25 °C

| complex | $[H^+]$, M | $[ClO_4^-]$, M | $[SO_4^{2-}]$, M | $I$, M | $k_1$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|
| $Co(NH_3)_5py^{3+}$ | neutral | 0.0 | 0.17 | 0.50 | $1.9 \times 10^5$ |
| | neutral | 1.0 | 0.33 | 2.0 | $2.0 \times 10^6$ |
| | 0.05 | 0.05 | 0.017 | 0.10 | $3.1 \times 10^5$ |
| | 0.05 | 1.0 | 0.33 | 2.0 | $3.1 \times 10^6$ |
| | 1.0 | 1.0 | 0.33 | 2.0 | $5.2 \times 10^6$ |
| $Co(NH_3)_6^{3+}$ | neutral | 1.0 | 0.33 | 2.0 | $1.4 \times 10^5$ |
| $Co(en)_3^{3+}$ | neutral | 0.0 | 0.17 | 0.50 | $1.3 \times 10^3$ |
| | neutral | 1.0 | 0.33 | 2.0 | $1.4 \times 10^4$ |

The majority of the rates could be measured by the stopped-flow technique. For the study of $Co(phen)_3^{3+}$, $Co(terpy)_2^{3+}$, and $Co(bpy)_3^{3+}$, $MV^{+}\cdot$ was generated by $e_{aq}^-$ reduction of $MV^{2+}$ (together with a small amount of Co(III) complex) within 1 μs. The OH and H radicals also produced in the pulse radiolysis were eliminated by inclusion of 5% *t*-BuOH.[14] The subsequent oxidation of $MV^{+}\cdot$ by each of the three cobalt(III) complexes present, in excess, was nicely first order (with half-lives in the 2–17-μs range). From the dependences of the first-order rate constants on [cobalt(III)], second-order rate constants $k_1$ would be calculated. All the results are collected in Table I. Most data were obtained at pH 7.2–7.8. Increasing the reaction pH to 9.2 had only a small effect on the rate constant (Table I). There were dramatic accelerating effects on the rates of the reactions of $MV^{+}\cdot$ when the ionic strength was increased by adding sodium perchlorate or perchloric acid (Table II and supplementary table). Reaction of $Co(diNOsar)^{3+}$ with $DQ^{+}\cdot$, $MDQ^{+}\cdot$, and $Co(sep)^{2+}$ was biphasic. The much faster of the two reactions corresponded to one-electron reduction of $Co(diNOsar)^{3+}$ to $Co(diNOsar)^{2+}$, and the rate constants for this are equated to $k_1$ and included in Table I. The subsequent reductions involved the $-NO_2$ groups. The fast absorbance change when $Co(diNOsar)^{3+}$ was mixed with $Co(sep)^{2+}$

$$Co(diNOsar)^{3+} + Co(sep)^{2+} \rightleftharpoons Co(diNOsar)^{2+} + Co(sep)^{3+} \quad k_2 \qquad (2)$$

was very small but was assigned to (2) because of the observed and anticipated absorbance increases at 360–400 nm and decreases at 470–500 nm.

## Discussion

Four of the five radicals produced by dithionite reduction of the viologen have spectral characteristics identical with those of

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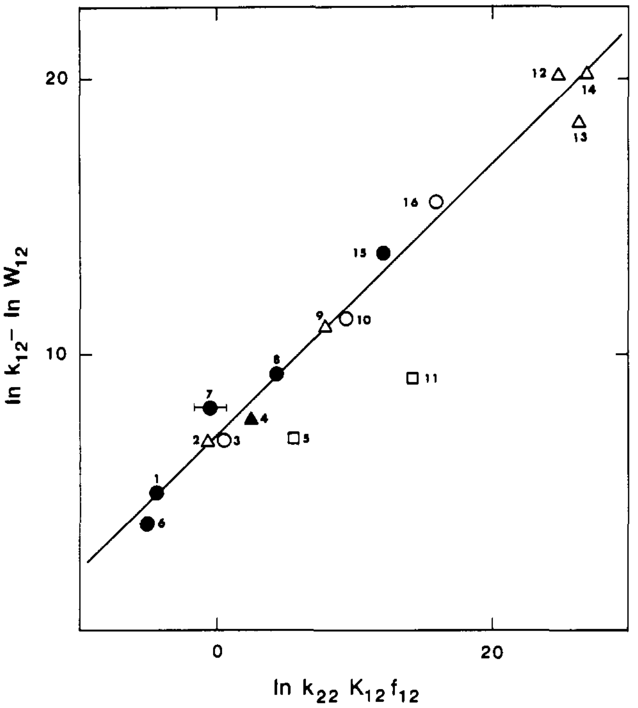

**Figure 1.** Plot of ln $k_{12}$ − ln $W_{12}$ vs. ln ($k_{22}K_{12}f_{12}$) for reactions of cobalt(III) complexes with viologen radicals: (1) $Co(en)_3^{3+}$–$DQ^{+}\cdot$; (2) $Co(en)_3^{3+}$–$MV^{+}\cdot$; (3) $Co(en)_3^{3+}$–$MDQ^{+}\cdot$; (4) $Co(en)_3^{3+}$–$PDQ^{+}\cdot$; (5) $Co(en)_3^{3+}$–$BDQ^{+}\cdot$; (6) $Co(chxn)_3^{3+}$–$DQ^{+}\cdot$; (7) $Co(NH_3)_6^{3+}$–$DQ^{+}\cdot$; (8) $Co(sep)^{3+}$–$DQ^{+}\cdot$; (9) $Co(sep)^{3+}$–$MV^{+}\cdot$; (10) $Co(sep)^{3+}$–$MDQ^{+}\cdot$; (11) $Co(sep)^{3+}$–$BDQ^{+}\cdot$; (12) $Co(bpy)_3^{3+}$–$MV^{+}\cdot$; (13) $Co(phen)_3^{3+}$–$MV^{+}\cdot$; (14) $Co(terpy)_2^{3+}$–$MV^{+}\cdot$; (15) $Co(diNOsar)^{3+}$–$DQ^{+}\cdot$; (16) $Co(diNOsar)^{3+}$–$MDQ^{+}\cdot$. The uncertainty in (7) arises from the possible range in value for $k_{22}$ of $10^{-7}$–$10^{-6}$ $M^{-1}$ $s^{-1}$.[19]

the species formed by $e_{aq}^-$ (pulse radiolytic) reduction of the viologen.[6,15] The species produced however by dithionite reduction of $BDQ^{2+}$ has a peak position (at 460 nm) markedly shifted from that reported for $e_{aq}^-$ reduction of $BDQ^{2+}$ (at 520 nm)[15] and confirmed by us.[6] Because of the uncertainty therefore in the nature of the radical produced by $S_2O_4^{2-}$ reduction of $BDQ^{2+}$, we examined the reduction of only two cobalt(III) complexes by this species (Table I). Similar rate constants were obtained for reduction of $Co(en)_3^{3+}$ by $MV^{+}\cdot$ and of $Co(NH_3)_5py^{3+}$ by $DQ^{+}\cdot$ and $MV^{+}\cdot$ when the radical was generated by dithionite reduction and by a photochemical reduction[13] of the oxidized viologen. In addition, our data with $Co(phen)_3^{3+}$, $Co(terpy)_3^{3+}$, and $Co(bpy)_3^{3+}$ oxidation of $MV^{+}\cdot$ generated by $e_{aq}^-$ reduction of the viologen are consistent with those of the other reductions (see Figure 1). We can be fairly certain, therefore, that we are examining the one-electron reduction of Co(III) complexes by the radicals $X^{+}\cdot$, when the latter are generated by dithionite reduction.

Reduction of $Co(diNOsar)^{3+}$ by viologen radicals, as well as by $Co(sep)^{2+}$, resembled the pattern previously reported for $S_2O_4^{2-}$ ion reduction of this Co(III) complex.[10] That is, rapid reduction of $Co(diNOsar)^{3+}$ to $Co(diNOsar)^{2+}$ occurred, and this was followed by reduction of the $-NO_2$ groups on the ligand with concomitant oxidation of cobalt(II) to cobalt(III).[10] Varying degrees of reduction, dependent on the viologen radical used, were observed, and these results and their associated kinetic behavior will be reported in a subsequent communication.

There are large effects of high $NaClO_4/HClO_4$ concentrations on the rates of $MV^{+}\cdot$ reactions (Table II). Böttcher and Haim generated $MV^{+}\cdot$ by reaction of $^*MV^{2+}$ with 2-propanol using flash photolysis. They reported a rate constant of $(1.2 \pm 0.3) \times 10^7$ $M^{-1}$ $s^{-1}$ at 23 °C and 1.0 M $HClO_4$ for the reduction of $Co(NH_3)_5py^{3+}$ by the $MV^{+}\cdot$ radical.[7] Our value is in good agreement with theirs. However, it appears that much of the nearly $10^2$ times faster rate in 1.0 M $HClO_4$ than in neutral solution residues in a high perchlorate concentration (Table II). This accelerating effect is also shown in the reaction of $MV^{+}\cdot$ with other cobalt(III) complexes. There are only small differences in the rate constants for reaction of $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_6^{3+}$ with $MV^{+}\cdot$ (or with $DQ^{+}\cdot$ and $SO_2^-$ ions).[16] A value of $5.1 \times 10^4$ $M^{-1}$ $s^{-1}$ was estimated for the reaction of $Co(en)_3^{3+}$ with $MV^{+}\cdot$, indirectly determined from the $MV^{2+}$-catalyzed reduction of $Co(en)_3^{3+}$ by $Eu^{2+}$ ion in $HClO_4$ medium.[8] Our value in 1.0 M $NaClO_4$ is in fair agreement.

**Table III.** Reduction Potentials, Radii, and Self-Exchange Rate Constants Used in Application of Eq 3–6

| reactant couple | $E°$, V | $10^8 \times r_{oxid}$,[a] cm | $10^8 \times r_{red}$,[b] cm | $k_{22}$, $M^{-1}$ $s^{-1}$ | $k_{11}$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|---|
| $Co(en)_3^{3+/2+}$ | −0.20[c] | 5.0 | 5.2 | $4.8 \times 10^{-5}$ [d] | |
| $Co(chxn)_3^{3+/2+}$ | −0.22[e] | 7.5[f] | 7.7 | $4.8 \times 10^{-5}$ [g] | |
| $Co(NH_3)_6^{3+/2+}$ | 0.06[h,i] | 3.5 | 3.7 | $10^{-7}$–$10^{-6}$ [i,j] | |
| $Co(diNOsar)^{3+/2+}$ | 0.04[k] | 5.5 | 5.7 | 0.25[l] | |
| $Co(sep)^{3+/2+}$ | −0.30[m] | 4.8 | 5.0 | 11.5[m] | |
| $Co(phen)_3^{3+/2+}$ | 0.42[n] | 7.0[o] | 7.0 | 40[p] | |
| $Co(terpy)_2^{3+/2+}$ | 0.27[q] | 7.0[o] | 7.0 | $4 \times 10^2$ [q] | |
| $Co(bpy)_3^{3+/2+}$ | 0.37[n] | 7.0[o] | 7.0 | 17[p] | |
| $Co(edta)^{-/2-}$ | 0.38[r] | 4.5 | 4.7 | $3.5 \times 10^7$ [s] | |
| $DQ^{2+/+}$ | −0.35[t] | 6.0 | 6.0 | | $10^8$ [u] |
| $MV^{2+/+}$ | −0.45[v] | 6.0 | 6.0 | | $10^8$ [u] |
| $MDQ^{2+/+}$ | −0.49[w] | 6.0 | 6.0 | | $10^8$ [u] |
| $PDQ^{2+/+}$ | −0.55[x] | 6.0 | 6.0 | | $10^8$ [u] |
| $BDQ^{2+/+}$ | −0.64[y] | 6.0 | 6.0 | | $5 \times 10^6$ [u] |

[a] van der Waals radius of sphere, of which longest axis of molecule is a diameter. [b] $0.2 \times 10^{-8}$ cm added to radius of corresponding cobalt(III) complex. [c] References 19, 21. [d] Reference 22. [e] Reference 23. [f] See also ref 24. [g] Assumed similar value to that for $Co(en)_3^{3+/2+}$. [h] Reference 25. [i] See discussion in ref 19. [j] Reference 26. [k] References 10, 17. [l] Estimated from $k_{12}$ for reaction 2. [m] References 19, 28. [n] Reference 29. [o] See also ref 30. [p] Reference 31. [q] References 30, 32. [r] Reference 33. [s] Reference 34. [t] References 12, 35, 36. [u] Calculated from cross-reactions between $MV^{2+}$ and $PDQ^{+}\cdot$ and between $MV^{2+}$ and $BDQ^{+}\cdot$.[6] [v] References 12, 35–37. [w] References 12, 38. [x] References 12, 35–37, 39. [y] References 12, 35, 36, 38.

There is a larger than $10^6$ difference in rate constants between the slowest and fastest reaction systems shown in Table I. Since these reactions are all undoubtedly outer sphere, because of the inert character of the cobalt(III) complexes examined and the nature of the reductants, we can apply the Marcus treatment.[17] Although the influence of work terms is small on these series of reactions at the high ionic strengths used, we have taken account of them and use the equations (3)–(6).[18-20] $k_{11}$ and $k_{22}$ are the

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \tag{3}$$

$$W_{12} = \exp[(w_{11} + w_{22} - w_{12} - w_{21})/2RT] \tag{4}$$

$$w_{ab} = \frac{4.2 \times 10^{-8} z_a z_b}{(r_a + r_b)[1 + 3.28 \times 10^7 (r_a + r_b) I^{1/2}]} \tag{5}$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln \dfrac{k_{11}k_{22}}{Z^2} + \dfrac{w_{11} + w_{22}}{RT}\right]} \tag{6}$$

self-exchange rate constants for the radical couple and the cobalt(III/II) redox couple, respectively. For the cross-reaction in ionic strength $I$, $k_{12}$ is the rate constant and $K_{12}$ is the equilibrium constant, estimated from the reduction potentials of the two couples. The reactant pairs have radii $r_a$ and $r_b$ (cm) and charges

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$z_a$ and $z_b$. $Z$ is the collision rate and is assumed to be $10^{11}$ M$^{-1}$ s$^{-1}$. Parameters used in the calculation of $W_{12}$ and $f_{12}$ are shown in Table III.[21-39] The self-exchange rate constants $k_{22}$ for the cobalt(III/II) complexes are well established, including $\mathrm{Co(NH_3)_6}^{3+/2+}$, which has been incorrectly assessed for some years.[19,26] We have indirectly determined the self-exchange rate constant for the $\mathrm{Co(diNOsar)}^{3+/2+}$ couple by studying the cross-reaction (2) and applying eq 3. The value (0.25 M$^{-1}$ s$^{-1}$) is similar to those determined for a variety of caged cobalt ions.[19] The self-exchange rate constant for the $\mathrm{Co(diNOsar)}^{3+/2+}$ couple was not determined directly by Sargeson and co-workers because of the difficulty of preparing the cobalt(II) complex,[19] although this has now been achieved.[11] For all viologen radicals, the radius was estimated to be $6.0 \times 10^{-8}$ cm, and the self-exchange rate constant $k_{11}$ was assigned the value $10^8$ M$^{-1}$ s$^{-1}$ (Table III).[6] Relatively large variations in these values only have a small effect on the magnitude of the work terms. The major modifying factor is $f_{12}$, and this is dominated by $K_{12}$, accurate values for which can be calculated from the established reduction potentials of the cobalt(III/II) and viologen/radical couples (Table III). From eq 3, plots of $\ln k_{12} - \ln W_{12}$ vs. $\ln (k_{22}K_{12}f_{12})$ should be linear with a slope 0.50. Such a plot for 16 of the reactions shown in Table I is displayed in Figure 1. The slope of the line is 0.49, and the value of $\ln k_{12} - \ln W_{12}$ is $0.5 \ln k_{11}$ when $\ln (k_{22}K_{12}f_{12}) = 0$. From the plot, $\ln k_{11} = 14.22$, whence $k_{11} = 1.5 \times 10^6$ M$^{-1}$ s$^{-1}$. This latter value for the self-exchange rate constants for the viologen/radical couples (all assumed to be similar) is in good agreement with that deduced ($8 \times 10^5$ M$^{-1}$ s$^{-1}$) from consideration of the rates of a number of reductions of $\mathrm{MV}^{2+}$ ion.[40] However, the study of the cross-reactions between $\mathrm{MV}^{2+}$ and $\mathrm{PDQ}^{+}\cdot$ and between $\mathrm{MV}^{2+}$ and $\mathrm{BDQ}^{+}\cdot$ by pulse-radiolytic methods indicate that the self-exchange rate constants for $\mathrm{MV}^{2+/+}$ and $\mathrm{PDQ}^{2+/+}$ are $\sim 10^8$ M$^{-1}$ s$^{-1}$ and that for $\mathrm{BDQ}^{2+/+}$ is 10–20 times less.[6] This may account for data points 5 and 11 being below the line. Recently, estimates of the $\mathrm{MV}^{2+}/\mathrm{MV}^{+}\cdot$ self-exchange rate constant ($5.4 \times 10^8$ M$^{-1}$ s$^{-1}$) in methanol by NMR line broadening[41] and of $\mathrm{X}^{2+}/\mathrm{X}^{+}\cdot$ ($\mathrm{X}^{2+}$ = 2,3,10,11-tetramethyldiquat, $5 \times 10^7$ M$^{-1}$ s$^{-1}$) in aqueous solutions by pulse-radiolytic methods[42] have been made. The plot in Figure 1 could be reconciled with a value of $k_{11} = 10^8$ M$^{-1}$ s$^{-1}$ by assigning a prefactor $p_{12}$ (which is essentially a transmission coefficient or perhaps a steric factor) value of 0.12 in the complete expression

$$k_{12} = p_{12}Z_{12}\exp(-\Delta G_{12}^{*}/RT) \qquad (7)$$

Lowered values for observed rate constants over those calculated for cross-reactions have often been observed.[43] For the $\mathrm{Co(edta)}^{-}$–$\mathrm{DQ}^{+}\cdot$ reaction, $\ln k_{12} - \ln W_{12} = 15.5$ and $\ln (k_{22}K_{12}f_{12}) = 9.0$. For the $\mathrm{Co(ox)_3}^{3-}$–$\mathrm{DQ}^{+}\cdot$ reaction, $\ln k_{12} - \ln W_{12} > 14.1$ and $\ln (k_{22}K_{12}f_{12}) = 13.1$. Both points are above the plot of Figure 1.

The reactions of $\mathrm{O_2}^{-}$ with a number of cobalt(III) complexes have been examined.[44-46] The second-order rate constants are as follows (M$^{-1}$ s$^{-1}$): 31.3, $\mathrm{Co(NH_3)_6}^{3+}$; 23.8, $\mathrm{Co(en)_3}^{3+}$; 16.4, $\mathrm{Co(chxn)_3}^{3+}$; $\sim 1$, $\mathrm{Co(sep)}^{3+}$; $7 \times 10^4$, $\mathrm{Co(terpy)_2}^{3+}$; $>10^4$, $\mathrm{Co(phen)_3}^{3+}$. There is a much larger range of rate constants for the reaction of $\mathrm{DQ}^{+}\cdot$ than of $\mathrm{O_2}^{-}$ with these complexes and only a weak correlation between their relative reactivities. Examination of the literature of reductions by the $\mathrm{SO_2}^{-}$ ion[10,16,45] shows that the viologen radicals $\mathrm{DQ}^{+}\cdot$ and $\mathrm{MV}^{+}\cdot$ and $\mathrm{SO_2}^{-}$ reduce $\mathrm{Co(NH_3)_6}^{3+}$, $\mathrm{Co(NH_3)_5py}^{3+}$, $\mathrm{Co(diNOsar)}^{3+}$, and $\mathrm{Co(terpy)_2}^{3+}$ with similar rate constants.

Finally, the rate constants for reduction of $\mathrm{Co(NH_3)_6}^{3+}$ by a series of nitrobenzoate and nitrogen heteroaromatic anion radicals have been determined.[47] In general, as expected, the rate constants increase as the reduction potential for the radical couple becomes more negative. For comparison, the rate constants for reduction of $\mathrm{Co(NH_3)_6}^{3+}$ by $^{-}\mathrm{O_2CC_6H_4NO_2}^{-}$ ($E° = -0.40$ V) is $1.2 \times 10^5$ M$^{-1}$ s$^{-1}$ at 22 °C, whereas that by $\mathrm{DQ}^{+}\cdot$ ($E° = -0.35$ V) is $5.0 \times 10^3$ M$^{-1}$ s$^{-1}$, slightly lower as a result of less-favorable electrostatics.

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**Registry No.** **1a**, 2764-72-9; **1b**, 16651-71-1; **1c**, 7325-63-5; **1d**, 16651-68-6; **2**, 4685-14-7; $\mathrm{Co(en)_3}^{3+}$, 14878-41-2; $\mathrm{Co(chxn)_3}^{3+}$, 41970-05-2; $\mathrm{Co(NH_3)_6}^{3+}$, 14695-95-5; $\mathrm{Co(NH_3)_5py}^{3+}$, 31011-67-3; $\mathrm{Co(sep)}^{3+}$, 72496-77-6; $\mathrm{Co(diNOsar)}^{3+}$, 85663-77-0; $\mathrm{Co(edta)}^{-}$, 15136-66-0; $\mathrm{Co(ox)_3}^{3-}$, 15053-34-6; $\mathrm{Co(phen)_3}^{3+}$, 18581-79-8; $\mathrm{Co(terpy)_2}^{3+}$, 19137-07-6; $\mathrm{Co(bpy)_3}^{3+}$, 19052-39-2.

**Supplementary Material Available:** Table containing the experimental kinetic data (4 pages). Ordering information is given on any current masthead page.

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