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Comparison of *N*,*N'*-Dimethyl-4,4'-bipyridinium Radical Ion and Excited Tris(2,2'-bipyridine)ruthenium(II) as Reductants of Various Substituted (Pyridine)pentaamminecobalt(III) Complexes

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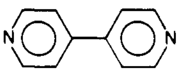
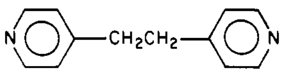
Methylviologen radicals have been generated via the reaction of $*MV^{2+}$ with 2-propanol under flash photolytic conditions. The rate constants for the reactions of MV^+ with pentaamminecobalt(III) complexes of pyridine, 1,2-bis(4-pyridyl)ethane, 4,4'-bipyridine, *trans*-1,2-bis(4-pyridyl)ethylene, and *N*-methyl-4,4'-bipyridine have been measured at 23 °C and 1.0 M $HClO_4$ and have the values 1.2×10^7, 1.8×10^7, 1.9×10^8, 2.7×10^8, and 1.8×10^8 $M^{-1}\ s^{-1}$, respectively. Two distinct mechanisms are proposed to account for the observed trends. For the two complexes that react at the lower rates, direct reduction of the cobalt(III) center is suggested. For the three complexes that react at the faster rates, the chemical mechanism is postulated, namely, initial, rate-determining reduction of the pyridine ligand, followed by very fast, intramolecular electron transfer from the reduced ligand to the cobalt(III) center.

Introduction

In previous work we sought evidence for the chemical mechanism of electron transfer[1] by exploiting the strong reducing properties of the excited state[2] of tris(2,2'-bipyridine)ruthenium(II), $*Ru(bp)_3^{2+}$. The oxidants were pentaamminecobalt(III) complexes containing an easily reduced ligand—a substituted pyridine[3] or a nitrobenzoate[4]—capable of yielding a relatively stable free radical. Although in neither case was a radical bound to the cobalt(III) center detected, the evidence for a chemical mechanism was rather convincing.[3,4] In the present paper, we report results of studies which provide additional support for the chemical mechanism. As oxidants we chose again the substituted-pyridine complexes



bpy



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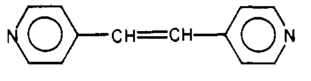

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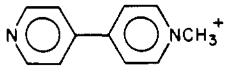

bpyMe

$Co(NH_3)_5L^{n+}$ (L = py, pyridine; bpy, 4,4'-bipyridine; bpa, 1,2-bis(4-pyridyl)ethane; bpe, *trans*-1,2-bis(4-pyridyl)ethylene; bpyMe, *N*-methyl-4,4'-bipyridine), for which we have extensive[3,5-7] information regarding their electron-transfer reactivity. For the reductant we chose the *N*,*N'*-dimethyl-4,4'-bipyridinium radical ion (hereafter abbreviated as MV^+, reduced methylviologen).[8] Methylviologen, MV^{2+}, the oxidized form of MV^+, is a very weak oxidant, and, therefore, solvent cage recombination effects, which gave rise to some difficulties in previous work,[4] are expected to be negligible. Moreover, there is current interest in MV^{2+} as a catalyst for the reduction of cobalt(III) complexes[9] and as an acceptor in charge-transfer complexes.[10,11] But, undoubtedly, the most notable feature of the chemistry of methylviologen is the publication explosion dealing with the utilization of $MV^{2+/+}$ couple as a relay in photochemical energy storage schemes.[12]

Experimental Section

Materials. The pyridine- and substituted-pyridine-pentaamminecobalt(III) complexes were the same samples used in previous work.[5,6,13] $[Ru(bp)_3]Cl_2$ (G.F. Smith) was converted to the corresponding perchlorate, which was then recrystallized twice from water. Methylviologen chloride (Aldrich) was purified by dissolution in ethanol followed by precipitation upon addition of acetone. The procedure was repeated three times. Solutions containing hexaaquovanadium(II) were obtained by dissolution of V_2O_5 in perchloric acid, followed by reduction of VO_2^+ with amalgamated zinc. Solutions of hexaaquovanadium(III) were obtained by anaerobic mixing of stoichiometric amounts of V^{2+} and VO_2^+. Lithium perchlorate (G. F. Smith) was recrystallized twice from water. The water and argon were purified as described previously.[4]

Kinetic Measurements. Two serum bottles, one containing the desired oxidant in 2.0 M $HClO_4$ and the other MV^+ at about 10^{-5} M (generated by treating MV^{2+} with amalgamated zinc) were connected by means of Teflon tubing to the anaerobic valve block of Durrum D-110 stopped-flow spectrometer. The solutions were transferred to the driving syringes by increasing the argon pressure in the serum bottles. Extensive oxygen leakage was minimized (but not entirely avoided) by sweeping the space behind the barrels of the driving syringes with argon. The disappearance of MV^+ was monitored at 603 nm, and pseudo-first-order rate constants were obtained from ln $(A_t - A_\infty)$ vs. t plots.

Flash-Photolysis Measurements. A solution containing approximately 2×10^{-5} M MV^{2+}, 0.10 M 2-propanol, 1.0 M $HClO_4$, and the desired oxidant (5×10^{-6}–10^{-2} M) was prepared in a serum bottle. Argon was bubbled through the solution for about 45 min, and then the solution was transferred to the photolysis cell (12.5 cm long) via a polyethylene tubing by increasing the argon pressure in the serum bottle. Following the flash (Xenon Corporation, Model 720 apparatus), the decrease in absorbance at 602 or 391 nm was followed as a function of time. From the absorbance changes, we estimate that the concentration of MV^+ produced in one flash was about 5×10^{-7} M. The concentration of the oxidant was a least 10 times greater than that of MV^+, and pseudo-first-order rate constants were obtained from ln $(A_t - A_\infty)$ vs. t plots. Blank experiments with the MV^{2+} omitted indicated no decomposition of the cobalt complexes under the flash photolytic conditions.

Results and Discussion

It has been shown that methylviologen radicals are produced efficiently by steady-state, UV irradiation of aqueous solutions

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containing MV^{2+} and a secondary alcohol.[14] The reaction sequence for 2-propanol is given by eq 1–3.[14] This method

$$MV^{2+} \xrightarrow{h\nu} {}^{*}MV^{2+} \qquad (1)$$

$$^{*}MV^{2+} + (CH_3)_2CHOH \rightarrow MV^{+} + (CH_3)_2COH + H^{+} \qquad (2)$$

$$(CH_3)_2COH + MV^{2+} \rightarrow (CH_3)_2CO + MV^{+} + H^{+} \qquad (3)$$

of generating MV^+ is quite convenient because the reactions are fast and irreversible. In the absence of oxidant, MV^+ accumulates in the solution,[14] but in the presence of oxidants, reaction 4 is expected to take place. In the present paper, we

$$MV^{+} + Ox \rightarrow MV^{2+} + Ox^{-} \qquad (4)$$

have exploited the sequence of eq 1–3 and the technique of flash photolysis to generate substantial concentrations of MV^+. Then, with the monitoring of the disappearance of the characteristic absorption of MV^+ at 603 or 391 nm,[8] direct kinetic measurements of reactions exemplified by eq 4 can be achieved. However, since this approach has not been utilized previously, we thought it prudent to test the method. First, solutions containing 2.0×10^{-5} MV^{2+}, 1.0 M $HClO_4$, and 0.10 M $(CH_3)_2CHOH$ were subjected to a series of successive flashes. The formation and disappearance of MV^+ was clearly indicated by the rise and decrease in absorbance at 603 or 391 nm. For the first three or four flashes, the half-life for the disappearance of MV^+ increased from several hundreds of microseconds to about 1 ms. After about a dozen flashes, the half-life stabilized at about 1 s. Presumably, during the first few flashes, residual oxygen and/or oxidizing impurities are consumed, and the 1-s half-life represents the intrinsic stability of MV^+ in 1.0 M $HClO_4$. Next, we measured the rate constant for the forward reaction in eq 5 by flash photolytic (FP)

$$V^{3+} + MV^{+} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} V^{2+} + MV^{2+} \qquad (5)$$

as well as stopped-flow (SF) techniques. At 25 °C, $[HClO_4] = 1.0$ M, $[V^{3+}] = 1.0 \times 10^{-3}$ M, and $[MV^+] \approx 10^{-5}$ M, we measured $k_5 = (2.0 \pm 0.3) \times 10^5$ M^{-1} s^{-1} by SF. At room temperature (ca. 23 °C), $[HClO_4] = 1.0$ M, $[(CH_3)_2CHOH] = 0.10$ M, and $[MV^{2+}] = 2.0 \times 10^{-5}$ M, $[V^{3+}] = (2.0\text{–}10) \times 10^{-4}$ M, we measured $k_5 = (1.7 \pm 0.3) \times 10^5$ M^{-1} s^{-1} by FP. The agreement between the two techniques established the validity of the flash photolysis of MV^{2+} in aqueous 2-propanol as a technique to generate MV^+ radicals and to measure rate constants for their reactions. Incidentally, our value of k_5 is not in good agreement with the value 9.4×10^4 M^{-1} s^{-1} calculated from the measured[9] value of k_{-5} (2.3 M^{-1} s^{-1} at 25 °C and 1.0 M $HClO_4$) and the value of the equilibrium constant calculated from the measured reduction potentials[9] of V^{3+} and MV^{2+}, −0.242 and −0.515 V, respectively. However, the value −0.242 V was obtained indirectly.[9] With the more generally accepted value −0.255 V, the calculated value for k_5 is 1.6×10^5 M^{-1} s^{-1}, which is within experimental error of our measured value.

The second-order rate constants for the reduction of the cobalt(III) complexes (eq 6) are listed in the second column

$$MV^{+} + Co(NH_3)_5L^{3+} \xrightarrow{H^+} MV^{2+} + Co^{2+} + 5NH_4^{+} + LH_2^{2+} \qquad (6)$$

of Table I. Each entry is the average of three to five experiments, covering a ca. 5-fold change in the concentration of the oxidant. Although the solutions were deaerated carefully, residual oxygen caused some difficulties because of its very rapid reaction[15] with MV^+. The rate of disappearance of MV^+ was somewhat faster for the first flash than for succeeding flashes, presumably because oxygen was present initially. After three or four flashes, the concentration of O_2 became too low to compete effectively with the cobalt(III) complex, and succeeding flashes gave the same rate within experimental error. The values reported in Table I were obtained usually after two or three flashes and are, as far as we can ascertain, free from the effect of O_2.

Table I. Rate Constants for Reduction of $Co(NH_3)_5L^{n+}$ Complexes by MV^+ and $^{*}Ru(bp)_3{}^{2+}$

L	k_{MV^+}, M^{-1} s^{-1} [a]	k_{Ru}, M^{-1} s^{-1} [b]
py	$(1.2 \pm 0.3) \times 10^7$	$(1.7 \pm 0.2) \times 10^8$
bpa	$(1.8 \pm 0.2) \times 10^7$	$(2.0 \pm 0.3) \times 10^8$
$bpMe^+$	$(1.8 \pm 0.2) \times 10^8$	$(1.1 \pm 0.1) \times 10^9$
bpy	$(1.9 \pm 0.2) \times 10^8$	$(5.7 \pm 0.6) \times 10^8$
bpe	$(2.7 \pm 0.4) \times 10^8$	$(1.2 \pm 0.1) \times 10^9$

[a] Measurements at 23 °C and 1.0 M $HClO_4$; present work. [b] Measurements at 23 °C, pH 5.6, and ionic strength 0.10 M; from ref 3.

Included in Table I for comparison purposes are the rate constants for the analogous reactions (eq 7) with the excited

$$^{*}Ru(bp)_3{}^{2+} + Co(NH_3)_5L^{3+} \rightarrow Ru(bp)_3{}^{3+} + Co^{2+} + 5NH_3 + L \qquad (7)$$

state of $Ru(bp)_2{}^{2+}$. The values listed are taken from our earlier work.[3] It will be seen that the reactivity pattern observed previously for the reduction of the pyridine- and substituted-pyridine–pentaamminecobalt(III) complexes by $^{*}Ru(bp)_3{}^{2+}$ is repeated for the corresponding reductions by the methylviologen radical, except that the reactivity range is somewhat larger for MV^+ (a factor of 2.2×10^2) than for $^{*}Ru(bp)_3{}^{2+}$ (a factor of 37). The observed trends are rationalized on the basis of two possible pathways[3] for the reduction of these cobalt(III) complexes: direct reduction of the cobalt(III) center (eq 8) or reduction of the bound pyridine ligand followed

$$Co^{III}(NH_3)_5L^{n+} + MV^{+} \rightarrow Co^{II}(NH_3)_5L^{(n-1)+} + MV^{2+} \qquad (8)$$

by rapid,[3,4] intramolecular electron transfer from the reduced ligand to the cobalt(III) center (eq 9 and 10). The relatively

$$Co^{III}(NH_3)_5L^{n+} + MV^{+} \rightarrow Co^{III}(NH_3)_5L^{(n-1)+}\cdot + MV^{2+} \qquad (9)$$

$$Co^{III}(NH_3)_5L^{(n-1)+}\cdot \rightarrow Co^{II}(NH_3)_5L^{(n-1)+} \qquad (10)$$

slow rates for $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5bpa^{3+}$ ($\sim 10^7$ M^{-1} s^{-1} for MV^+ and $\sim 10^8$ M^{-1} s^{-1} for $^{*}Ru(bp)_3{}^{2+}$) are taken to be indicative of direct reduction of the cobalt(III) center, whereas the faster rates of $Co(NH_3)_5(bpy)Me^{4+}$, $Co(NH_3)_5bpy^{3+}$, and $Co(NH_3)_5bpe^{3+}$ ($\sim 2 \times 10^8$ M^{-1} s^{-1} for MV^+ and $\sim 10^9$ M^{-1} s^{-1} for $^{*}Ru(bp)_3{}^{2+}$) are considered diagnostic of reduction of the heterocyclic ligand. To be sure, the above mechanistic assignment is consistent with the known relative ease of reduction of the pyridine ligands. The reduction of py (and presumably bpa) by MV^+ or $^{*}Ru(bp)_3{}^{2+}$ is thermodynamically unfavorable,[16] whereas the reductions of bpy, $bpyMe^+$, and bpe are exoergonic for $^{*}Ru(bp)_3{}^{2+}$ and (presumably) ergo neutral for MV^+. Therefore, for $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5bpa^{3+}$ the chemical mechanism is precluded, and the (relatively slow) reduction of the cobalt(III) center occurs. In contrast, for $Co(NH_3)_5bpy^{3+}$, $Co(NH_3)_5bpe^{3+}$, and $Co(NH_3)_5bpyMe^{4+}$, reduction of the pyridine ligand is feasible and the chemical mechanism obtains, the rate being substantially higher than the rate at which the

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cobalt(III) center is reduced directly.

The faster rate for the complexes for which the chemical mechanism has been postulated could hardly be explained on the basis of direct electron transfer into cobaltIII) orbitals since their acceptor properties are not expected to change by changing the substituents in the pyridine ring. This expectation is based on the insensitivity of the rates of reaction of the cobalt(III) complexes to the nature of the pyridine ligand when the reductant is too weak to reduce the ligands.[13,17,18] Rate constants for internal electron transfer in the ion pairs $\mathrm{Co(NH_3)_5L^{n+}|Fe(CN)_6^{4-}}$ are in the narrow range $(1.0\text{–}5.0) \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ for L = py, bpa, bpy, bpyMe$^+$, nicotinamide, and isonicotinamide, to be contrasted with the wider range $(1.2\text{–}27) \times 10^{7}\ \mathrm{M^{-1}\ s^{-1}}$ for the analogous reductions by MV$^+$.[19] $\mathrm{Fe(CN)_6^{4-}}$ is too weak a reductant to respond to variations in the acceptor abilities of the bound ligands, and the range of rates is taken to be a measure of the effect of the pyridine ring substituents on the acceptor properties of the cobalt(III) orbitals. Therefore, the considerably larger range of rates for MV$^+$ is interpreted on the basis of an additional reaction pathway at the upper rate range, namely, the increasing ability of the ligand to act as the primary electron acceptor.

Additional evidence for the proposed mechanistic assignment comes from a comparison between MV$^+$ and $^{*}\mathrm{Ru(bp)_3^{2+}}$ as reductants toward the pyridine complexes. The ratios of the rate constants for $^{*}\mathrm{Ru(bp)_3^{2+}}$ to the rate constants for MV$^+$ are in the range 11–14 for the cobalt complexes reacting via the direct mechanism, whereas the ratios are in the range 3–6 for the complexes reacting via the chemical mechanism. If all the complexes underwent reaction by the same mechanism, the reactivity ratio of $^{*}\mathrm{Ru(bp)_3^{2+}}$ to MV$^+$, based on the Marcus theory, would be expected to be independent of the cobalt(III) complex. The fact that two different ranges of reactivitiy ratios are observed supports the suggestion that two distinct mechanisms, reduction of the cobalt(III) center or reduction of the pyridine ligand, are operative in the present systems.

Finally, it is noteworthy that the rates of reduction of the (pyridine)pentaamminecobalt(III) complexes by MV$^+$ exhibit a general tendency toward increasing as the length of the pyridine ligand increases.[20] For the direct reduction of the cobalt(III) center via the pyridine ligand, the opposite trend is observed and expected on theoretical grounds.[21] Therefore, we consider these observations, although the argument is indirect, as a reinforcement of the dual mechanistic assignment proposed for the reduction of the (pyridine)pentaamminecobalt(III) complexes by MV$^+$ and $^{*}\mathrm{Ru(bp)_3^{2+}}$.

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Registry No. MV$^+$, 25239-55-8; $\mathrm{Ru(bp)_3^{2+}}$, 15158-62-0; $\mathrm{Co(NH_3)_5py^{3+}}$, 31011-67-3; $\mathrm{Co(NH_3)_5bpa^{3+}}$, 38671-05-5; $\mathrm{Co(NH_3)_5bpyMe^{4+}}$, 66290-41-3; $\mathrm{Co(NH_3)_5bpy^{3+}}$, 53879-90-6; $\mathrm{Co(NH_3)_5bpe^{3+}}$, 61177-69-3.

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(18) We also wanted to obtain the rate constants for the reduction of the pyridine complexes by $\mathrm{Ru(NH_3)_6^{2+}}$. Experiments with $\mathrm{Co(NH_3)_5py^{3+}}$ confirmed the literature value. However, the reaction with $\mathrm{Co(NH_3)_5bpy^{3+}}$ displayed an autocatalytic behavior, even at pH 7.0. Moreover, we found that added free bpy had a catalytic effect on the $\mathrm{Co(NH_3)_5py^{3+}\text{–}Ru(NH_3)_6^{2+}}$ reaction. Therefore, these studies did not yield the desired rate constants.

(19) The range of rates for $^{*}\mathrm{Ru(bp)_3^{2+}}$, $(1.7\text{–}11) \times 10^{9}\ \mathrm{M^{-1}\ s^{-1}}$, is about as narrow as the range for $\mathrm{Fe(CN)_6^{4-}}$. However, at the upper range of the $^{*}\mathrm{Ru(bp)_3^{2+}}$ reactions, the rate constants are approaching the diffusion-controlled limit within a factor of 3.

(20) Note that because of its higher positive charge the complex $\mathrm{Co(NH_3)_5bpMe^{4+}}$ cannot be compared, without first making an electrostatic correction, with the other complexes.

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Optical Activity of Tetrahedral Dihalo[(−)-α-isosparteine]cobalt(II) Complexes

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The absorption and circular dichroism spectra of the tetrahedral halide complexes $[\mathrm{Co}(l\text{-}\alpha\text{-isp})\mathrm{X_2}]$ have been recorded over the range of the d–d transition manifold, 2000–20 000 cm^{-1}. An interaction between the C–H stretching vibration transitions of the organic ligand and the electronic d–d transitions of the metal ion is observed in the optical activity near 2900 cm^{-1}. The spectra are discussed in terms of the dynamic ligand-polarization mechanism for d–d transition probabilities.

Introduction

Hitherto, the investigation of the optical activity of chiral transition-metal complexes has been confined largely to the type of chelated coordination compound first optically resolved by Werner.[1] These enantiomers are mainly six-coordinate complexes of the M(III) ions with a d^3 or spin-paired d^6 configuration, which affords an orbitally nondegenerate ground state, and with ligands at a position in the spectrochemical series that corresponds to d–d absorption in the readily accessible visible or quartz UV region. The principal features of the d–d absorption and circular dichroism (CD) spectra of the dihedral (D_3) tris-chelate transition-metal complexes were early established,[2,3] and the first quantum-mechanical interpretation of d-electron optical activity, employing crystal field theory, was based upon the CD spectra of these complexes.[4]

Crystal field theory proved to have a limited application to the analysis of d–d optical activity. A pseudoscalar crystal field, required for a first-order d–d rotational strength, was found[5] to give a vanishing contribution in a chiral complex with octahedral coordination, while the corresponding second-order approach gave crystal field d–d rotational strengths at variance with the observed CD spectra of D_3 tris-chelate complexes.[6] An alternative treatment of d–d optical activity, based upon

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