$(H_2O)_6^{3+}$ remained, and disproportionation of the Rh(II) generated is possible. As an alternative, evolution of O_2 was tested for by passing N_2 gas through the reactant mixture and then into Cr^{2+} or a solution of the sepulchrate cage complex $[Co(sep)]^{2+}$.[12] No O_2 was detected by this procedure.

Reactions of Anions with Rh_2^{4+}. With Cl^-, Br^-, I^- and sulfate at concentrations in the range $(2–5) \times 10^{-4}$ M, and $[Rh_2^{4+}] = (0.5–2.0) \times 10^{-3}$ M, $[H^+] = 0.5–1.0$ M, and $I = 1.0$ M ($LiClO_4$), Rh metal formation was observed. A yellow precipitate was obtained with thiocyanate, which is probably a μ-thiocyanato polymer. No substitution reactions could be monitored.

Discussion

Figure 2 for the Cr^{2+} reduction of $[Rh(H_2O)_6^{3+}]$ clearly implicates $RhOH^{2+}$ as reactant with little or no contribution from the path involving the hexaaqua ion. From an acid-dissociation pK_a of 3.4 for $[Rh(H_2O)_6]^{3+}$,[10,13] a true rate constant for the path involving Cr^{2+} reduction of $RhOH^{2+}$ is 2.3×10^5 M^{-1} s^{-1}. The Cr^{2+} reductions of RhX^{2+} ions ($X^- = OH^-, Cl^-, Br^-$) can be formulated as involving outer-sphere electron transfer (4) followed by (5), or inner-sphere electron transfer (6) followed by (7). In

$$Cr^{2+} + RhX^{2+} \rightarrow Cr(III) + Rh^{2+} + X^- \qquad (4)$$

$$2Rh^{2+} \rightarrow Rh_2^{4+} \qquad (5)$$

$$Cr^{2+} + RhX^{2+} \rightarrow (CrXRh)^{4+} \qquad (6)$$

$$2(CrXRh)^{4+} \rightarrow 2CrX^{2+} + Rh_2^{4+} \qquad (7)$$

the case of the Cr^{2+} reduction of $[Rh(H_2O)_6]^{3+}$ no effect of $[Cr(H_2O)_6]^{3+}$ (0.03 M) in supressing formation of Rh^{2+} in (4) by the back-reaction was noted (Table I). Moreover with $RhCl^{2+}$ and $RhBr^{2+}$ it has been demonstrated that $CrCl^{2+}$ and $CrBr^{2+}$ are products.[2,4] Had Cl^- and Br^- been released as free anions, then reaction with the Rh_2^{4+} product would have resulted in formation of Rh metal. Also, the pronounced $[H^+]^{-1}$ dependence for the Cr^{2+} reduction of $[Rh(H_2O)_6]^{3+}$ carries the implication of an inner-sphere reaction involving $RhOH^{2+}$. Outer-sphere reactions would not discriminate as markedly between the aqua and hydroxo forms.[14]

Different behavior is observed with V^{2+} as reductant, when Rh metal is formed.[1] Previous work has demonstrated a clear preference of V^{2+} for outer-sphere electron-transfer pathways.[15] The fact that a $(CrXRh)^{4+}$ binuclear intermediate is generated in (6) presumably stabilizes the Rh^{2+} until dimerization to Rh_2^{4+} can occur. The formation of Rh metal in the V^{2+} reaction is consistent with an outer-sphere reaction as in (4), which generates monomeric Rh^{2+}. Since O_2 formation was not detected, disproportionation of Rh^{2+} to Rh metal and Rh(III) is likely as the dominant process. We have not been able to quantity any of these processes, and although Rh(III) is formed, this may not be a clean reaction with formation of only $[Rh(H_2O)_6]^{3+}$. It is possible that addition of coordinating anions to Rh_2^{4+} results in the formation of increasing amounts of monomeric Rh^{2+} due to a weakening of the Rh–Rh bond, and hence Rh metal is formed. Addition of another d^7 ion, Co^{2+} (up to 0.03 M), has no influence on either the Cr^{2+} or V^{2+} reductions of $[Rh(H_2O)_6]^{3+}$. Here the stabilization of Rh^{2+} by formation of a $(RhCo)^{4+}$ dimer was considered possible. That no such effect is observed suggests that the 2+ ions do not have a sufficient affinity for each other (in accordance with the observation that Co^{2+} does not itself dimerize).

Finally the order of effectiveness of the bridging halide ions $Br^- > Cl^-$ in the Cr^{2+} reduction of RhX^{2+} is consistent with the normal order of effectiveness $I^- > Br^- > Cl^-$ of halide ions, which has been observed previously in other metal ion redox processes.[16]

Acknowledgment. We are grateful to the SERC for a studentship (to E.F.H.), to the British Council for financial support, and to Wroclaw University in Poland for leave of absence (to M.M.). We also wish to acknowledge the helpful collaboration of Professor J. J. Ziolkowski and the loan of rhodium compounds from Johnson Matthey Chemicals.

Registry No. $[Rh(H_2O)_6]^{3+}$, 16920-31-3; $[Rh(H_2O)_5Cl]^{2+}$, 15696-62-5; $[Rh(H_2O)_5Br]^{2+}$, 48019-52-9; Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; Rh_2^{4+}, 55569-94-3; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; SO_4^{2-}, 14808-79-8.

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Mechanism of Electron Transfer to Pentaammine(pyridine)cobalt(III) Complexes by Aliphatic Radicals, Hexaaquovanadium(II), and Hexaammineruthenium(II) Ions

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The rates of electron transfer to a series of pentaammine(pyridine)cobalt(III) complexes, $Co(NH_3)_5(NC_5H_4X)^{3+}$ (X = 3-CN, 3-Cl, H, 4-CH_3, 4-$C(CH_3)_3$, and 4-$N(CH_3)_2$), have been determined. A kinetic competition method based on the homolytic scission of the chromium–carbon bond in $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was used to evaluate rate constants for the reducing agent $\cdot C(CH_3)_2OH$, whereas direct measurements were carried out for the reductions by $V(H_2O)_6^{2+}$ and $Ru(NH_3)_6^{2+}$. In all three cases the rate constants show mild and similar sensitivity to the substituent on the pyridine ring. The variations are well correlated by the Hammett equation, the reaction constants being 1.1, 1.3, and 1.5, respectively. Arguments are advanced that in each case the reactions proceed by direct outer-sphere electron transfer to the cobalt(III) and not by a "chemical mechanism" entailing prior electron transfer to the pyridine ring.

Introduction

The mechanism by which an electron donor (reducing agent) reacts with a suitable acceptor has been widely explored in the case where both are transition-metal complexes. More specifically, outer-sphere electron-transfer constitutes one large, well-recognized, and extensively studied group of reactions.[2-6]

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Electron-transfer reactions in which the donor is a free radical, potentially a very large group of reactions, have been studied much less extensively. That is not to say that such data are entirely lacking; indeed, extensive compilations of available kinetic data have recently been published.[7,8] Rather, it seems that the shortcoming is 2-fold. First, the same oxidizing agents have not always been used for both classes of donors, often because of practical limitations accompanying the different experimental techniques. Second, objective criteria are needed to assess whether the mechanisms are or are not the same.

Free-radical donors, like transition-metal complexes, can and do react by outer-sphere electron transfer. This is very likely the preferred mechanism for both types of reductants with substitutionally inert oxidants. Of course, if the metal center is not readily reducible, the free-radical donor may react by an alternative pathway. Free radicals often possess standard reduction potentials much more negative than those of the customarily studied metal ion reductants. Thus an additional and possibly more effective channel for the free radical may be opened if the oxidizing partner has a suitable ligand acceptor.

The title complex, $Co(NH_3)_5py^{3+}$, reacts with conventional mild reductants $M^{II}L_6^{2+}$, (e.g. $Cr(H_2O)_6^{2+}$, $V(H_2O)_6^{2+}$, Eu_{aq}^{2+} and $Ru(NH_3)_6^{2+}$) by simple outer-sphere electron transfer.[9,10] It is also known to be reduced by the aliphatic radical $\cdot C(CH_3)_2OH$, an exceptionally powerful reductant ($E° \sim -1.2$ V vs. NHE[11]), yielding Co^{2+}.[12,13]

With the development of a kinetic competition technique[14-18] that permits the determination of a wide range of rate constants for the reactions of substrates with aliphatic radicals, provided the substrates do not rapidly react with Cr^{2+}, it becomes possible to extend in a substantive way the range of data available. Although not a panacea, the kinetic competition method bypasses some of the limitations and complications of other methods[14-18] for assessing free-radical rate constants, such as those inherent in the use of pulse radiolysis and product-yield methods such as continuous radiolysis. This permits us to address the questions formulated above, by use of a homologous series of oxidizing agents that react with ML_6^{2+} ions as well as with reducing aliphatic radicals.

That is not to say, however, that the mechanisms have to be the same. Indeed, the very reason that free pyridinium ions are known to be rapidly reduced by $\cdot C(CH_3)_2OH$ is what makes this particular series of cobalt complexes of interest. They pose just that feature we seek to explore: the ligand and the metal are each, independently, known to be reduced by this radical, as in pyH^+ [15,19] and $Co(NH_3)_6^{3+}$.[14] The question is as follows: When the two are combined, how, in general, can one determine which event occurs, and what is the correct answer in this case?

Table I. Characterizations of the Prepared $[(NH_3)_5Co(NC_5H_4X)](ClO_4)_3$

X	λ_1(max)/nm[a]	λ_2(max)/nm (ϵ/M^{-1} cm^{-1})	% Co found (calcd)
3-CN	476	339 (55)	9.8 (10.8)
3-Cl	476	340 (66)	10.6 (10.6)
H	475[b]	340 (52)[b]	... (11.3)
4-CH_3	476	340 (60)	8.2 (11.0)
4-$C(CH_3)_3$	478	340 (57)	10.0 (10.2)
4-$N(CH_3)_2$	485	345[c]	9.8 (10.4)

[a] ϵ at $\lambda_1 = 61.2 \pm 0.6$ M^{-1} cm^{-1} for all complexes. [b] Values quoted in ref 6: ϵ/M^{-1} cm^{-1} = 63.8 at 475 nm and 54.4 at 340 nm. [c] Shoulder.

With these objectives in mind, we present here the results of mechanistic investigations concerning $Co(NH_3)_5py^{3+}$ and a series of meta-and para-substituted derivatives. We consider reactions of $\cdot C(CH_3)_2OH$ (eq 1) and ML_6^{2+} (eq 2, $ML_6^{2+} = V(H_2O)_6^{2+}$ and $Ru(NH_3)_6^{2+}$) and the correlation of the substituent effects

$$Co(NH_3)_5py^{3+} + \cdot C(CH_3)_2OH \rightarrow Co(NH_3)_5py^{2+} + (CH_3)_2CO + H^+ \quad (1)$$

$$Co(NH_3)_5py^{3+} + ML_6^{2+} \rightarrow Co(NH_3)_5py^{2+} + ML_6^{3+} \quad (2)$$

for each reactant separately and for the given systems with one another. We also compare these results to those for $Co(NH_3)_6^{3+}$, a complex in which the "chemical mechanism", (i.e., ligand reduction) cannot occur.

Experimental Section

Materials. The sample of $[(NH_3)_5CoNC_5H_5](ClO_4)_3$ was prepared, largely as described in the literature,[9] by heating the pentaammine aquo complex with pyridine in *N,N*-dimethylformamide and then precipitating the product with sodium perchlorate. The product was purified by recrystallization from 0.1 M perchloric acid. Its purity and identity were checked by cobalt analysis[20] and by the position and molar absorptivities of the UV/visible absorption maxima, as given in Table I. Substituted complexes were prepared analogously; even if previously unreported, they are straightforward extensions of a known preparation, and thus the same characterization methods sufficed.

Solutions of $V(H_2O)_6^{2+}$ were prepared by reduction of vanadyl(2+) perchlorate, obtained in solution from the reaction of vanadyl sulfate with barium perchlorate, all analytical grade, over amalgamated zinc. The concentration of $V(H_2O)_6^{2+}$ was determined spectrophotometrically at 850 nm (ϵ 3.22 M^{-1} cm^{-1}).[21] Solutions of $Cr(H_2O)_6^{2+}$ were also prepared by zinc reduction. 2-Propanol was distilled before use and redistilled weekly or as necessary. It was stored as much as possible out of direct light to prevent formation of impurities (peroxides), which interfered with its use in the preparation of organochromium complexes by the modified Fenton-reaction method, eq 3.[22]

$$2Cr(H_2O)_6^{2+} + H_2O_2 + (CH_3)_2CHOH + H^+ = Cr(H_2O)_6^{3+} + (H_2O)_5CrC(CH_3)_2OH^{2+} + 3H_2O \quad (3)$$

Commercial $[Ru(NH_3)_6]Cl_3$ was recrystallized several times according to the literature procedure.[23] Its concentration was determined spectrophotometrically at 390 nm ($\epsilon = 35$ M^{-1} cm^{-1}).[24] Other reagents were reagent grade commercial products or were obtained by routine methods. Many of the reagents, and all of the chemical reactions investigated, are highly sensitive to traces of molecular oxygen; thus the measurements were conducted by syringe–septa methods under an atmosphere of chromous-scrubbed nitrogen.

Techniques. Kinetic investigations were made by using conventional UV/visible spectrophotometry with Cary Models 219 and 17 instruments, which are equipped with thermostated cell compartments. The reactions of the free radical were followed by monitoring the decrease of the

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Table II. Ranges of the Concentrations Used and the Slopes of $(k_{obsd} - k_A)^{-1}$ vs. $[Cr^{2+}]/[Co(III)]$ Plots Obtained for the Reduction of $(NH_3)_5Co(NC_5H_4X)^{3+}$ Complexes by the 1-Hydroxy-1-methylethyl Radicals[a]

X	$10^4 \times [Cr^{2+}]/M$	$10^4 \times [Co(III)]/M$	$[Cr^{2+}]/[Co(III)]$	slope/s[b]
3-CN	3.49–6.21	9.96–1.75	0.35–3.55	2.83 ± 0.23
3-Cl	2.57–6.0	8.50–1.46	0.30–3.16	13.1 ± 0.4
H	2.0–12.3	14.7–1.41	0.135–3.60	33.4 ± 0.6
$4-CH_3$	2.87–4.73	7.0–2.4	0.53–1.97	43.2 ± 1.9
$4-C(CH_3)_3$	2.29–6.48	6.6–2.3	0.45–2.56	46.1 ± 1.0
$4-N(CH_3)_2$	1.23–4.39	6.3–2.5	0.21–1.59	117.0 ± 2.7

[a] 25 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol. [b] Uncertainties quoted are the standard deviations.

absorbance of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ at or near its absorption maximum at 311 nm (ϵ 700 M^{-1} cm^{-1}). (Actually, to optimize absorbance changes, a wavelength between 300 and 330 nm was selected for any given cobalt complex, depending on its spectrum and concentration.) The kinetic studies were conducted in solutions containing known and relatively high and constant concentrations of $Cr(H_2O)_6^{2+}$ and cobalt(III); the concentration of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was much lower. The data in each run followed pseudo-first-order kinetics, and rate constants were evaluated by standard methods.

The reactions of the cobalt complexes with $V(H_2O)_6^{2+}$ and $Ru(NH_3)_6^{2+}$ were followed at 475 nm, at or near the absorption maxima of the cobalt(III) complexes (see Table I). The complex was the limiting reagent in each run, and the ML_6^{2+} was present in relatively high and constant concentrations. A first-order kinetic analysis was also applicable to these data.

Results

Reduction of Cobalt(III) Complexes by $\cdot C(CH_3)_2OH$. The reactions that are important in this chemistry are the same set found in earlier work[14] relating to $Co(NH_3)_6^{3+}$. The chemical equations are given in eq 4–6; note that the bimolecular self-reactions of radicals are unimportant throughout, since the rapid reactions in eq 5 and 6 maintain the free radical at a low, steady-state concentration. Except for k_R, the rate constants k_A, k_H, and k_{Cr} are known from earlier work.[14,22,25]

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + (CH_3)_2CHOH \quad (k_A) \tag{4}$$

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_2O \rightleftarrows Cr(H_2O)_6^{2+} + \cdot C(CH_3)_2OH \quad (k_H,\ k_{Cr}) \tag{5}$$

$$\cdot C(CH_3)_2OH + (NH_3)_5Co(py)^{3+} \rightarrow (CH_3)_2CO + H^+ + (NH_3)_5Co(py)^{2+} \quad (k_R) \tag{6}$$

$$(NH_3)_5Co(py)^{2+} + 6H_3O^+ \xrightarrow{\text{fast}} Co(H_2O)_6^{2+} + 5NH_4^+ + pyH^+ \tag{7}$$

Under all the reaction conditions investigated, application of the steady-state approximation to the concentration of $\cdot C(CH_3)_2OH$ is an excellent approximation. In those circumstances, the rate expression for the disappearance of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ is

$$\frac{-d[(H_2O)_5CrC(CH_3)_2OH^{2+}]}{dt} = \left(k_A + \frac{k_H k_R[Co^{III}]}{k_R[Co^{III}] + k_{Cr}[Cr^{2+}]}\right)[(H_2O)_5CrC(CH_3)_2OH^{2+}] \tag{8}$$

Provided $[(NH_3)_5Co(py)^{3+}]$ and $[Cr(H_2O)_6^{2+}]$ are high relative to $[(H_2O)_5CrC(CH_3)_2OH^{2+}]$, which is the case here, the reaction will be expected to follow a pseudo-first-order rate equation. This is what was found in all cases experimentally. The kinetic data are summarized in Table II, which gives the ranges of concentrations used in each set of measurements.[26] As expected, the experimental rate constants vary with the concentrations of the excess reagents. Consistent with the model of eq 4–6, the lower limit is k_A, the rate constant for acidolysis of the organochromium cation, and is approached at relatively high $[Cr(H_2O)_6^{2+}]$ and low $[(NH_3)_5Co(py)^{3+}]$. The upper limit of the pseudo-first-order rate constant is $k_A + k_H$, which is the situation that results at low $[Cr(H_2O)_6^{2+}]$ and high $[(NH_3)_5Co(py)^{3+}]$, such that both reactions of $(H_2O)_5CrC(CH_3)_2OH^{2+}$, acidolysis and homolysis, can occur.

Table III. Rate Constants for the Reduction of $(NH_3)_5Co(NC_5H_4X)^{3+}$ Complexes by 1-Hydroxy-1-methylethyl Radicals, $V(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ [a]

X	$k_R/M^{-1}\ s^{-1}$	$k_V/M^{-1}\ s^{-1}$ [b]	$k_{Ru}/M^{-1}\ s^{-1}$ [b]	σ[c]
3-CN	1.42×10^8	2.83	20.5	+0.56
3-Cl	3.1×10^7	0.76	7.0	+0.37
H	1.2×10^7	0.27[d]	1.15[d]	0
$4-CH_3$	9.3×10^6			−0.17
$4-C(CH_3)_3$	8.7×10^6	0.18	0.98	−0.20
$4-N(CH_3)_2$	3.4×10^6	0.032	0.16	−0.83

[a] 25 °C, $[H^+] = 0.1$ M, $\mu = 1.0$ M ($HClO_4 + LiClO_4$), with aqueous 1 M 2-propanol for k_R, and purely water for k_{Ru} and k_V. [b] $[H^+] = 0.01$ M, μ adjusted by HCl + LiCl. [c] Hammett σ values. [d] $k_V = 0.24$ M^{-1} s^{-1} at $[H^+] = 1.0$ M and $\mu = 1.1$ M (ClO_4^-) and $k_{Ru} = 0.67$ M^{-1} s^{-1} at $[H^+] = 0.013$ M and $\mu = 0.5$ M (Cl^-) have been reported in ref 10.

The rate constant k_A, applicable at a given $[H^+]$, is available from published data[14,22,27] and was also redetermined during the course of these investigations. It is given by the expression $k_A/s^{-1} = 3.31 \times 10^{-3} + 4.91 \times 10^{-3}\ [H^+]$, which provides the numerical value suitable for any given experiment. Analysis of the kinetic data (k_{obsd} as functions of $[Cr(H_2O)_6^{2+}]$ and $[(NH_3)_5Co(py)^{3+}]$) was done by use of a least-squares program. The indicated least-squares analysis then afforded values of the composite quantity of $k_{Cr}/k_H k_R$. The least-squares values of this composite, designated S, are shown in the last column of Table II. Aside from the variation of k_A with $[H^+]$, a minor contribution to k_{obsd} in any event, the reaction rates and the values of the parameter S are independent of $[H^+]$ in the range 0.1–0.5 M.

To extract the desired rate constant k_R from each set of data it is necessary to use values of the rate constants k_H and k_{Cr} available from the literature, as follows: $k_H = 0.127$ s^{-1},[22] a value also redetermined here, and $k_{Cr} = 5.1 \times 10^7$ M^{-1} s^{-1}.[25,28] The resulting second-order rate constants k_R for the reactions under investigations are summarized in Table III.

It is useful to consider the same set of data from a graphical point of view, to display the range of reaction rates and the concentration dependences. For that purpose the expression for k_{obsd} can be rearranged to the following form:

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_R k_H}\,\frac{[Cr(H_2O)_6^{2+}]}{[(NH_3)_5Co(py)^{3+}]} \tag{9}$$

According to this relation, the inverse of the rate enhancement over acidolysis, i.e. $(k_{obsd} - k_A)^{-1}$, should vary linearly with the ratio of the concentrations of the two metal complexes that compete for the free radical. Such plots for all of the cobalt(III) complexes investigated are shown in Figure 1. As predicted, they have a common intercept, k_H^{-1}, but have slopes S that differ from one cobalt(III) complex to the next. The steepest slope is for the complex having the lowest reactivity with $\cdot C(CH_3)_2OH$, and vice versa.

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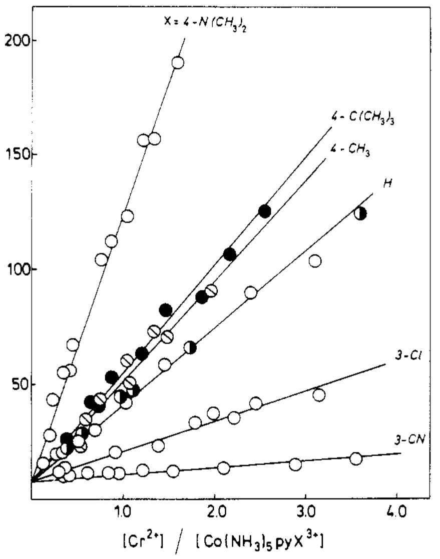

Figure 1. Plots of $(k_{obsd} - k_A)^{-1}$ vs. $[Cr^{2+}]/[Co^{III}]$ for the reductions of $(NH_3)_5Co(NC_5H_4X)^{3+}$ complexes by 2-hydroxy-2-propyl radicals at 25 °C, $[H^+] = 0.100$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol. The substituents X are indicated in the figure. For X = H, the points symbolized as ◑ refer to $[H^+] = 0.500$ M.

Stoichiometry of the Reactions between $(NH_3)_5Co(py)^{3+}$ and $\cdot C(CH_3)_2OH$. To confirm that these reactions do, indeed, occur as written in eq 1, the yield of Co^{2+} was determined[20] in several instances. The value of $[Co^{2+}]$ found is to be compared to $[\cdot C(CH_3)_2OH]_0$ in the given experiment. Since the free radical is not added as such, the expected value of its initial concentration must be determined from the concentrations of $Cr(H_2O)_6^{2+}$ and H_2O_2 used in the preparation of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. Ideally (eq 3), the effective value of $[\cdot C(CH_3)_2OH]_0$ would be equal to $[H_2O_2]_0$, were it not for several complicating features. One complication is that only 86% of the reaction of $HO\cdot$ and $(CH_3)_2CHOH$, a key step leading to $(H_2O)_5CrC(CH_3)_2OH^{2+}$ in the modified Fenton method, leads to the desired α radical $\cdot C(CH_3)_2OH$, the balance resulting in the β aliphatic radical (13%) and the oxy radical (ca. 1%).[29] The consequence in this work is that $[(H_2O)_5CrC(CH_3)_2OH^{2+}]$ is, at most, 86% of $[H_2O_2]_0$. In practice, it is even somewhat lower (typically 70–80%) owing to minor but appreciable side reactions, including radical disproportionation and outer-sphere oxidation of $Cr(H_2O)_6^{2+}$. Once formed, not all of the organochromium cation $(H_2O)_5CrC(CH_3)_2OH^{2+}$ yields the free radical $\cdot C(CH_3)_2OH$. As indicated in eq 4–6, the actual proportion of homolysis depends on the values of all four rate constants and varies from run to run, as a function of $[(NH_3)_5Co(py)^{3+}]$ and $[Cr(H_2O)_6^{2+}]$. With those concentrations given in a particular experiment, it is thus possible to use the indicated considerations to estimate to an adequate degree of precision the expected, effective value of $[\cdot C(CH_3)_2OH]_0$, for purposes of comparison with the experimental value of Co^{2+} in that determination. The Co^{2+} ion produced was determined for the reaction of $(NH_3)_5Co(3\text{-}CNpy)^{3+}$ and $(NH_3)_5Co((4\text{-}(CH_3)_3C)py)^{3+}$. An amount equivalent to $[\cdot C(CH_3)_2OH]_0$ was found.

Reduction of Cobalt(III)–Pyridine Complexes by ML_6^{2+}. Reactions of the series of $(NH_3)_5Co(py)^{3+}$ complexes with $V(H_2O)_6^{2+}$ and $Ru(NH_3)_6^{2+}$ are quite straightforward. The literature contains numerous examples of such data. For that reason, it sufficed to conduct but two or three kinetic determinations at varying $[ML_6^{2+}]$ for any given reaction. Each experiment afforded a pseudo-first-order rate constant; the quotient of $k_{obsd}/[ML_6^{2+}]$ represents the second-order rate constant for reaction 2. These values proved to be independent of $[ML_6^{2+}]$, confirming the second-order kinetic expression. The rate constants so determined are designated k_V and k_{Ru} for the respective reducing agents.

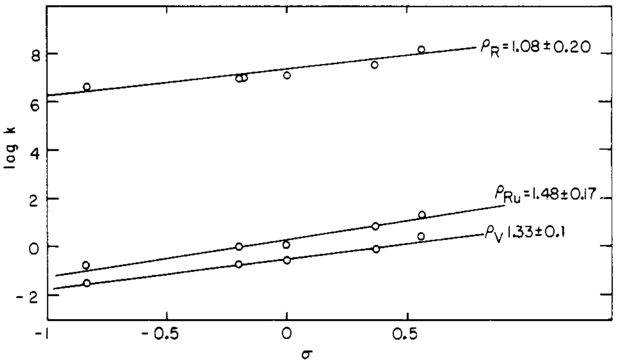

Figure 2. Plots of the logarithm of the rate constants for the reduction of $(NH_3)_5Co(NC_5H_4X)^{3+}$ complexes by 2-hydroxy-2-propyl radicals (k_R), hexaaquovanadium(II) ions (k_V), and hexammineruthenium(II) ions (k_{Ru}) vs. the Hammett σ values for the substituents X of the coordinated pyridine ligand.

Table III summarizes the values of k_V and k_{Ru} for all of the complexes investigated.

Discussion

These results establish that aliphatic radicals react directly with this series of cobalt(III) complexes, yielding Co^{2+} as in eq 1. This is in keeping with an earlier report,[12] although the rate constant estimated for the parent complex from G values in continuous radiation chemistry ($\sim 10^9$ M^{-1} s^{-1}) is significantly different from the value we have found (1.2×10^7 M^{-1} s^{-1}), determined more directly from a kinetic competition method. We note, however, that the rate constants for the reduction of $(NH_3)_5Co(NC_5H_4X)^{3+}$ by $\cdot C(CH_3)_2OH$ are higher than those for either of its constituents alone, pyridines and $Co(NH_3)_6^{3+}$. This synergism is probably related to the effect of pyridines on the reduction potential of the Co(III) center.

Substituent Effects. The reaction rates change perceptibly but not dramatically with substituents added to the pyridine ring. The rate effects caused by these substituents are the same in direction and similar in magnitude for all three reductants. The direction of the effect is such that the reaction rate increases with the electron-withdrawing character of a substituent, and vice versa. This trend is consistent with these being reactions in which an electron is added to the cobalt complex, since one would anticipate that the removal of electron density would, indeed, accelerate this type of overall reaction.

Hammett Equation Analysis. The variation between the rate extremes amounts to a factor of 42 for $\cdot C(CH_3)_2OH$, 88 for $V(H_2O)_6^{2+}$, and 128 for $Ru(NH_3)_6^{2+}$. The Hammett equation of physical organic chemistry can provide one approach to the analysis of these results. Figure 2 shows the analysis of the substituent effects in terms of a plot of log k vs. the Hammett substituent constant for the given group X. Data for all three of the reactions are shown, and it can be seen that each follows a linear relation and thus is well correlated by the Hammett equation

$$\log k_x = \sigma\rho + \log k_0 \qquad (10)$$

Least-squares analysis of these data give the following values for the reaction constants ρ in each case: $\cdot C(CH_3)_2OH$, 1.1 ± 0.2; $V(H_2O)_6^{2+}$, 1.3 ± 0.1; $Ru(NH_3)_6^{2+}$, 1.48 ± 0.17.

The result that the kinetic data fit the Hammett relation suggests that the reactions are controlled in a general way by the electron density at the reaction center and that specific substituent effects, such as steric influences, are minimal. In no case, therefore, is electron transfer at the periphery of the pyridine ring a likely reaction pathway.

Another LFER Analysis. One method of comparison that has been especially useful in earlier work[10,30,31] has been an exami-

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[29] Asmus, K.-D.; Möckel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

[30] Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769.

[31] Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 394.

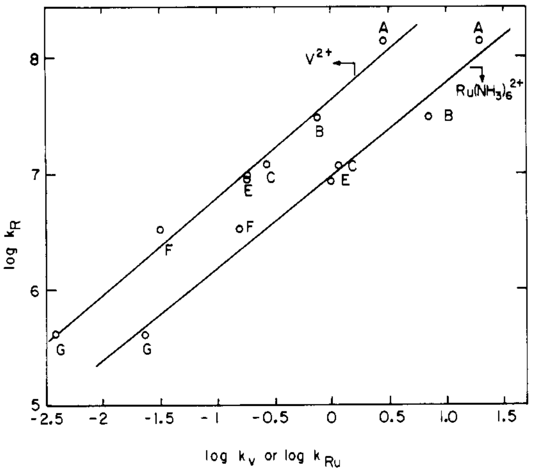

Figure 3. Plots of logarithm of the rate constants for the reductions of $(NH_3)_5Co(NC_5H_4X)^{3+}$ complexes by 2-hydroxy-2-propyl radicals (k_R) vs. log (k_V) for the reductions of the same complexes by hexaaquovanadium(II) ions and vs. log (k_{Ru}) for the reductions by hexaammineruthenium(II) ion at 25 °C, $\mu = 1.0$ M ($HClO_4 + LiClO_4$). The pyridine substituents are (A) 3-CN, (B) 3-Cl, (C) H, (E) 4-$C(CH_3)_3$, and (F) 4-$N(CH_3)_2$; point G refers to $Co(NH_3)_6^{3+}$.

nation of whether or not the rates of reduction of a given series of complexes by two different metals (M and N) are correlated. This correlation, when it is successful, often takes the form of a relation such as $\log k_M = m \log k_N + b$. This treatment permits the inclusion of related oxidants that are not members of the family of substituted pyridine derivatives, such as $Co(NH_3)_6^{3+}$ and $Co(en)_3^{3+}$. Thus data applying to these complexes, otherwise not part of the Hammett relation, can be included as a part of the analysis of the mechanism.

Figure 3 shows such correlations for the present series of reactions in terms of plots of log k_R vs. log k_V and log k_{Ru}. Both sets of data define reasonable straight lines, which are given by

$$\log k_R = (0.84 \pm 0.05) \log k_V + 7.65 \pm 0.07 \qquad (11)$$

$$\log k_R = (0.80 \pm 0.06) \log k_{Ru} + 6.99 \pm 0.06 \qquad (12)$$

Mechanism and Conclusion. The following facts are germane to the assignment of a reaction mechanism: (1) All of the electron donors show strikingly similar substituent effects as expressed by the Hammett equation. (2) The rates of electron transfer from the aliphatic radical, although much faster than from the metal ion donors, are very successfully correlated with one another in terms of LFER relations. (3) The latter treatment readily and quantitatively incorporated kinetic data for complexes with an "innocent" ligand in place of the pyridine, for which electron transfer to the ligand is clearly impossible. (4) Reduction of free pyridinium ions by $\cdot C(CH_3)_2OH$ occurs at rates which are also correlated by the Hammett expression with $\rho = 8.5$ for a limited series of substituents.[15] The difference in the sensitivity of the reactions of free and complexed pyridines to substituent effects implies a mechanistic difference between the two series.

These facts, considered as a whole, suggest to us that each of the reactions proceeds by rate-limiting electron transfer to the cobalt itself. The comparisons cited above would appear to rule out a pathway consisting of a "chemical mechanism" by which electron transfer occurs first to pyridine. These results do suggest further experiments, however, which are presently in progress; in that work we plan to investigate reactions in which the pyridine is bound to a metal center that is not capable of further reduction, (e.g., $(NH_3)_5Ru(py)^{2+}$) or to one that can be reduced only at much more negative potentials, (e.g., $(H_2O)_5Cr(py)^{3+}$). Reduction of the pyridine ring will necessarily be involved if reaction occurs in the former case, and it may also occur in the latter. As such, the rates would be expected to respond to substituents differently, perhaps more in parallel to the trends reported[15] for $C_5H_4NH^+$ and $C_5H_4NCH_3^+$. Such a duality of mechanisms, i.e. outer-sphere electron transfer vs. attack at the ligand, has been observed recently in the reaction of alkyl radicals with $M(phen)_3^{3+}$ (M = Fe, Ru, Os; phen = 1,10-phenanthroline).[32,33]

Acknowledgment. This work was supported in part by the U.S. Department of Energy through the Joint U.S.-Yugoslav Board for Scientific Cooperation, by the Research Council (SIZ-II) of S.R. Croatia, and by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. $Co(NH_3)_5(NC_5H_4\text{-}3\text{-}CN)^{3+}$, 80041-64-1; $Co(NH_3)_5(NC_5H_4\text{-}3\text{-}Cl)^{3+}$, 99618-38-9; $Co(NH_3)_5(NC_5H_5)^{3+}$, 31011-67-3; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}CH_3)^{3+}$, 33248-50-9; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}C(CH_3)_3)^{3+}$, 99618-39-0; $Co(NH_3)_5(NC_5H_4\text{-}4\text{-}N(CH_3)_2)^{3+}$, 99618-40-3; $\cdot C(CH_3)_2OH$, 5131-95-3; $V(H_2O)_6^{2+}$, 15696-18-1; $Ru(NH_3)_6^{2+}$, 19052-44-9.

Supplementary Material Available: Tables of kinetic data for each reaction (4 pages). Ordering information is given on any current masthead page.

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[32] Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.

[33] We are grateful to a reviewer for bringing this point to our attention.

Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

A High-Valent Dioxoruthenium(VI) Complex of 2,2′-Bipyridine (bpy)—Preparation and Characterization of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$

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The preparation and characterization of *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ (bpy = 2,2′-bipyridine) are described. The observed high $E_f°$ value (1.25 V vs. NHE) for the *trans*-$[Ru^{VI}(bpy)_2O]_2^{2+}$/*trans*-$[Ru^{IV}(bpy)_2O(OH_2)]^{2+}$ couple indicates that *trans*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ is potentially useful for the photocatalytic splitting of water to oxygen.

Introduction

High-valent oxo complexes of ruthenium, especially those containing polypyridyl ligands, are of current interest in view of their potential usefulness as oxidative catalysts.[1] Although monooxoruthenium(IV) species are well-known,[2] the existence of dioxoruthenium(VI) species of 2,2′-bipyridine (bpy), namely *cis*-$[Ru^{VI}(bpy)_2O_2]^{2+}$ [3a] and *trans*-$[Ru^{VI}(bpy)O_2Cl_2]$,[3b] has been reported only on several occasions. However, no detailed spectroscopic characterizations on this class of dioxo complexes have

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[1] See, for example: Gerstein, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029–4030.

[2] See, for example: Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106–4115.

[3] (a) Takeuchi, K. J.; Samuels, G. J.; Gerstein, S. W.; Gilbert, J. A.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1407–1409. (b) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315–1320.

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