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Oxidation of Ruthenium(II) Ammine Complexes by 1-Hydroxy-1-methylethyl Radicals and by Tris(bipyridyl)cobalt(III) Ions

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The kinetics of oxidation of $Ru(NH_3)_6^{2+}$ and of $(NH_3)_5Ru(NC_5H_4X)^{2+}$, X = H, 3-Cl, 4-$CH_3$, 4-$C(CH_3)_3$, and 4-$N(CH_3)_2$, by $^{\bullet}C(CH_3)_2OH$ (k_R) and by $Co(bpy)_3^{3+}$ (k_{Co}) have been evaluated. Values of log k_R vary linearly with log k_{Co}. The individual values of log k_R and log k_{Co} are both correlated by the Hammett σ parameters, the reaction constants being $\rho = -0.50 \pm 0.03$ and -1.9 ± 0.1, respectively. The reactions of all the Ru(II) complexes with $^{\bullet}C(CH_3)_2OH$ are acid-catalyzed ($k_R = k_{R0} + k_{R1}[H^+]$), an unprecedented observation. This suggests the rate-limiting step is solvolysis of an ion-paired successor complex, $\{RuL_6^{3+},{}^{-}C(CH_3)_2OH\}$, with H_2O and H_3O^+ each being solvolytically active.

Introduction

An aliphatic, hydroxylated, carbon-centered free radical such as $^{\bullet}C(CH_3)_2OH$ can function as both an electron donor ($^{\bullet}C(CH_3)_2OH \rightarrow (CH_3)_2CO + H^+ + e^-$) and an electron acceptor ($^{\bullet}C(CH_3)_2OH + H^+ + e^- \rightarrow (CH_3)_2CHOH$). The first mode tends to predominate for this particular radical, a very potent electron donor ($E° \approx -1.3$ V). Published kinetic data for a considerable number of such reactions have recently been tabulated.[2,3] For example, ruthenium(III) complexes, such as $Ru(NH_3)_6^{3+}$, are quite rapidly reduced, as shown in eq 1.[2,4,5]

$$Ru(NH_3)_6^{3+} + {}^{\bullet}C(CH_3)_2OH \rightarrow Ru(NH_3)_6^{2+} + (CH_3)_2CO + H^+ \quad (1)$$

The prevalence of reduction reactions makes it difficult to study the *oxidations* by this radical. That is, the oxidation of a ruthenium(II) complex (eq 2) would be followed immediately by its rereduction (eq 1).[6,7]

$$Ru(NH_3)_6^{2+} + {}^{\bullet}C(CH_3)_2OH \xrightarrow{H^+} Ru(NH_3)_6^{3+} + (CH_3)_2CHOH \quad (2)$$

No kinetic data, to our knowledge, have been reported for the oxidation of ruthenium(II) complexes by these radicals.[8] This reaction (eq 2) and others similar to it cannot be studied by standard methods, in which a "burst" of the radical is generated. This system is, however, ideally constituted to take advantage of the kinetic method[9,10] that we have termed the method of "stored free radicals".[9-11] This method is based upon homolysis of the organochromium(2+) complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$.

In the case of $(NH_3)_5Ru(py)^{2+}$ (py = pyridine), the pyridine ligand might function as an electron acceptor, as it does in the case of $(H_2O)_5Cr(py)^{3+}$,[11] which undergoes a reaction with $^{\bullet}C(CH_3)_2OH$. Here the metal center plays an incidental role. On the other hand, the metal center might function as an electron donor, as with $Ru(NH_3)_6^{2+}$ in eq 2, leaving no evident role for the pyridine, itself then a bystander. We present evidence that the latter situation prevails.

Table I. Spectral Characterization of the Prepared $[(NH_3)_5Ru(NC_5H_4X)](ClO_4)_2$

X	λ(max)/nm ($10^{-3}\epsilon/M^{-1}$ cm^{-1}) λ_1	λ_2
4-$N(CH_3)_2$	350 (7.4)	258 (12.2)
4-$C(CH_3)_3$	399 (7.7)	244 (4.46)
4-CH_3	397 (7.7)	244 (4.5)
H	407 (7.7)	244 (4.9)
3-Cl	426 (7.9)	256 (4.6)

To learn how the ruthenium(II) complexes are oxidized by the radical, we consider the kinetic effects of ring substitution on the pyridine ligand, as compared to the inductive effect of the substituent and its effect on the Ru(III)/Ru(II) reduction potentials. For calibration purposes, kinetic data were also obtained for reactions of the ruthenium(II) complexes with the outer-sphere oxidant $Co(bpy)_3^{3+}$ (bpy = bipyridyl). Unlike the Ru(II)–Co(III) reaction, that between the ruthenium(II) complexes and the aliphatic radical does not occur by simple electron transfer. The formation of a free carbanion can be excluded on thermodynamic grounds.

We sought to learn how such reactions occur from an examination of the effects of $[H_3O^+]$ and from deuterium kinetic isotope effects. The strong π interactions with suitable acceptors in $Ru(NH_3)_5L^{2+}$ complexes can clearly influence the reactivity and must be considered in any analysis of the mechanism.

Experimental Section

Materials. The samples of pentaammine(substituted pyridine)ruthenium(II) perchlorate, $[(NH_3)_5Ru(NC_5H_4X)](ClO_4)_2$, were prepared by a slightly modified literature method.[12] A suspension of 0.3 g of $[(NH_3)_5RuCl](ClO_4)_2$ in 10–15 mL of water was reduced over zinc amalgam under argon in the presence of 30 mmol of the desired pyridine ligand for approximately 40 min at room temperature. The ruthenium(II) complex was precipitated from the homogeneous product solution by saturated $NaClO_4$ solution. The crude product had to be recrystallized at least three times and usually four or five times from 50:50 methanol–water solution at 50 °C to obtain consistent kinetic results since unreacted ruthenium(III) or left-over free pyridine ligand was shown to catalyze the loss of $CrC(CH_3)_2OH^{2+}$ under the required reaction conditions. The exceptional purity of the Ru(II) complexes is needed only for the "stored free radical" method used to study the reactions of $^{\bullet}C(CH_3)_2OH$ and not for the $Co(bpy)_3^{3+}$ reactions, for which ordinary purity suffices.

The identities of the ruthenium(II) complexes were ascertained by their UV/visible absorption maxima shown in Table I. The positions and molar absorptivities of the maxima are in very good agreement with the literature for the known complexes.[13] The spectra of the air-sensitive complexes were determined under air-free conditions.

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[7] The oxidation of Eu^{2+} by this radical was successfully studied,[6] despite this limitation because the concentration imbalance (in these experiments, $[Eu^{2+}] \gg [Eu^{3+}]$) was sufficient to assist in overcoming the limitation and also because the two rate constants are not inordinately different. In contrast, the rate constants for the ruthenium complexes in eq 1 and 2 appear to be greatly in favor of the former, $k_1 \gg k_2$.

[8] The addition of α-hydroxyalkyl radicals to the polypyridine ligands of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ has been observed: Venturi, M.; Emmi, S.; Fuochi, P. G.; Mulazzani, Q. G. *J. Phys. Chem.* **1980**, *84*, 2160.

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$[(NH_3)_5Ru(py)](ClO_4)_3$ was prepared from the ruthenium(II) pyridine complex by the published procedure.[14] The product was recrystallized from 0.1 M $HClO_4$ and quantitatively identified by reduction over zinc amalgam to the corresponding (starting) $[(NH_3)_5Ru(py)]^{2+}$ complex.

A solution of the ruthenium(II) pyridine complex containing deuteriated ammonia, $[(ND_3)_5Ru(py)]^{2+}$, was prepared by reducing the ruthenium(III) complex in 99.8% deuteriated water (Aldrich), as described by Meyer and Taube.[15] $[Co(bpy)_3](ClO_4)_3$ was prepared from $CoCl_2$ and 2,2′-bipyridine by the method of Burstall and Nyholm.[16] The spectrum (λ_{max} 450 nm, ϵ 68.9 M^{-1} cm^{-1}) agreed well with literature data.[17]

Commercial $[Ru(NH_3)_6]Cl_3$ (Strem) was recrystallized according to the published procedure.[18] Solutions of $Cr(H_2O)_6^{2+}$ were prepared by reducing $Cr(H_2O)_6^{3+}$ over zinc amalgam. 2-Propanol was redistilled as necessary, at least weekly. Commercial $[Ru(NH_3)_5Cl]Cl_2$ (Strem) was used for preparative purposes without further purification. The pyridines (Merck or Fluka) were repeatedly distilled or recrystallized before further preparative work. The stock solution of lithium perchlorate was the same as in a previous study.[11] The organochromium complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was prepared from the reaction between chromium(II) ions and hydrogen peroxide as previously described.[19] All other chemicals used were analytical grade. Redistilled water was used throughout. Oxygen-sensitive solutions were handled by syringe–septa methods under argon that had been passed over a heated copper catalyst and scrubbed through a Cr^{2+} solution.

Techniques. Kinetics of the reaction between the ruthenium(II) complexes and the 1-hydroxy-1-methylethyl radical were studied by conventional UV–visible spectrophotometry with a Cary 219 or Cary 17 instrument. As described previously,[20] a decrease in the absorbance of $CrC(CH_3)_2OH^{2+}$, which is homolyzed to yield the free radical, was monitored at its absorption maximum, 311 nm (ϵ = 2500 M^{-1} cm^{-1}). Pseudo-first-order kinetics were assured by having concentrations of the reactants competing for the radical, $Cr(H_2O)_6^{2+}$ and $(NH_3)_5Ru(NC_5H_4X)^{2+}$, at concentrations substantially higher than that of $CrC(CH_3)_2OH^{2+}$.

The level of the ruthenium(II) concentration was limited by its high contribution to the absorbance of the reaction mixture at the monitoring wavelength. No interference from the reduction of ClO_4^- by the ruthenium(II) complexes was observed, since that reaction is slow in comparison with the reactions of interest.

Ruthenium(II) was injected last into a solution prepared by dissolving a solid sample of the complex in deaerated water before each run. The solutions of $[Ru(NH_3)_6](ClO_4)_3$ were reduced over zinc amalgam before injection, and the same procedure was applied to the 4-(dimethylamino)pyridine complex. The less air sensitive complexes $(NH_3)_5Ru(4\text{-}CH_3\text{-}py)^{2+}$ and $(NH_3)_5Ru(4\text{-}t\text{-}Bu\text{-}py)^{2+}$ were injected either with or without previous treatment over zinc amalgam, with the same kinetic results. The $(NH_3)_5Ru(4\text{-}(CH_3)_2N\text{-}py)^{2+}$ ion undergoes an acid-catalyzed change, probably aquation, which interfered with the kinetics of interest in 10^{-2} M H^+. Its reaction with the radicals was therefore evaluated at 2×10^{-4} M H^+, where no interference was observed, as also confirmed by blank experiments.

The pseudo-first-order kinetics of the reaction between ruthenium(II)–pyridine complexes and $Co(bpy)_3^{3+}$ were monitored at the absorption maxima (380–426 nm) of the ruthenium(II) complexes in the presence of much higher concentrations of cobalt(III), by using the stopped-flow apparatus[21] previously described.

Results

Reactions with $^{\bullet}C(CH_3)_2OH$: Stoichiometry. Although it was expected that oxidation of the ruthenium(II) center by the radical would be preferred over reduction of the coordinated pyridine ligand, stoichiometry experiments for the reaction of $(NH_3)_5Ru(py)^{2+}$ and $(NH_3)_5Ru(3\text{-}Cl\text{-}py)^{2+}$ were performed to prove the point. Reaction mixtures of (8–9) $\times 10^{-5}$ M $(H_2O)_5CrC(CH_3)_2OH^{2+}$, $\sim 2 \times 10^{-4}$ M Cr^{2+}, and $\sim 2 \times 10^{-4}$ M $(NH_3)_5Ru(py)^{2+}$ or $(NH_3)_5Ru(3\text{-}Cl\text{-}py)^{2+}$ in 0.10 M H^+ and μ = 0.1 M ($LiClO_4$) were monitored spectrophotometrically at the absorption maximum of the ruthenium(II) complex (407 or 426 nm). The slight change of absorbance noted over the course of time corresponded merely to that associated with the depletion of the organochromium cation. Since its acidolysis (eq 3) is minimal and radical disproportionation negligible under the circumstances,[19,20] the amounts of radicals consumed by the ruthenium(II) complex in eq 5 are very nearly equal to the amount of the organochromium complex (eq 4).

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+} + (CH_3)_2CHOH \quad k_A{}^{19} \quad (3)$$

$$(H_2O)_5CrC(CH_3)_2OH^{2+} + H_2O \rightleftarrows Cr(H_2O)_6^{2+} + {}^{\bullet}C(CH_3)_2OH \quad k_H,\ k_{Cr}{}^{19,20,22} \quad (4)$$

$$(NH_3)_5Ru(py)^{2+} + {}^{\bullet}C(CH_3)_2OH \xrightarrow{H^+} (NH_3)_5Ru(py)^{3+} + (CH_3)_2CHOH \quad k_R \quad (5)$$

All of the ruthenium(II) complex oxidized by the radicals in eq 5 is recovered by reduction of the ruthenium(III) complex, either with chromium(II) or with the radical itself (eq 6 and 7, respectively). Under the conditions employed, eq 7 is prevalent

$$(NH_3)_5Ru(py)^{3+} + Cr(H_2O)_6^{2+} \rightarrow (NH_3)_5Ru(py)^{2+} + Cr(H_2O)_6^{3+} \quad k_6 \quad (6)^{23}$$

$$(NH_3)_5Ru(py)^{3+} + {}^{\bullet}C(CH_3)_2OH \rightarrow (NH_3)_5Ru(py)^{2+} + (CH_3)_2CO + H^+ \quad k_7 \quad (7)^{5}$$

although both reactions occur to an appreciable extent, as considered subsequently.

Regardless of the extent of each, however, the ruthenium(II) complex should be (and is) quantitatively recovered at the end. Were the radicals instead to reduce the coordinated pyridine ligand to the dihydropyridine, then the strong metal-to-ligand charge-transfer absorptions of the ruthenium(II) complexes at 407 and 426 nm would be significantly altered, contrary to the constancy observed.

Kinetics. The principles and practice of the kinetic method have been described previously.[20] Application of the steady-state approximation to the concentration of $^{\bullet}C(CH_3)_2OH$ yields the expression for the rate of disappearance of the organochromium ion given in eq 8. (Actually, eq 8 is rigorously correct only if eq 6 predominated over eq 7, as discussed subsequently.)

$$-d[(H_2O)_5CrC(CH_3)_2OH^{2+}]/dt = \left\{k_A + \frac{k_H k_R[RuL_6{}^{2+}]}{k_R[RuL_6{}^{2+}] + k_{Cr}[Cr^{2+}]}\right\}[(H_2O)_5CrC(CH_3)_2OH^{2+}] \quad (8)$$

With $[RuL_6{}^{2+}]$ and $[Cr^{2+}]$ significantly higher than $[CrC(CH_3)_2OH^{2+}]$, the term is parentheses becomes a pseudo-first-order rate constant, represented as k_{obsd}. The term may be rearranged to eq 9. The spontaneous acidolysis rate constants,

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_R k_H}\,\frac{[Cr(H_2O)_6{}^{2+}]}{[RuL_6{}^{2+}]} \quad (9)$$

$k_A/s^{-1} = 3.31 \times 10^{-3} + (4.91 \times 10^{-3})[H^+]$,[19] were calculated for the acidities used, and the first-order rate constants, k_{obsd}, observed for each individual run were treated according to eq 9. The data are depicted in Figures 1 and 2. The range of ratios of $[Cr^{2+}]/[RuL_6{}^{2+}]$ used in the runs and shown in Figures 1 and 2 was limited on one side by the slowness of the process studied as compared to the rate of the spontaneous acidolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ and on the other by the background absorbance of the ruthenium(II) complexes. The slopes of the straight lines obtained by plotting $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[RuL_6{}^{2+}]$ were calculated with a least-squares program and are

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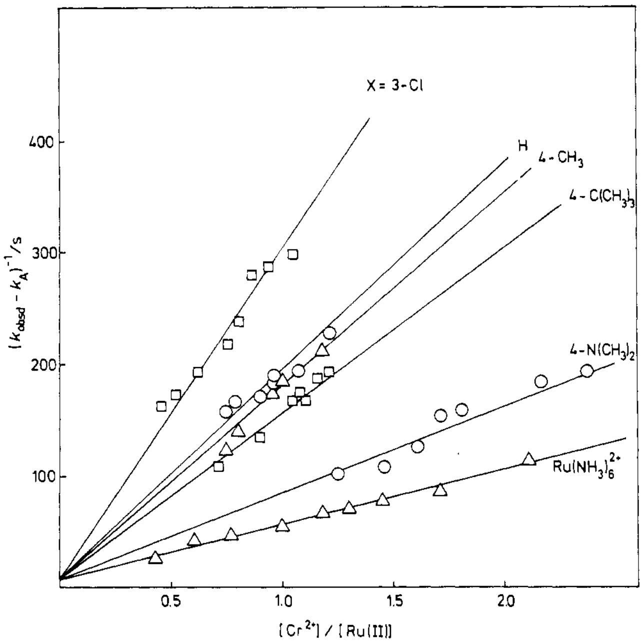

Figure 1. Plots of $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[Ru(II)]$ for the oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ and $Ru(NH_3)_6^{2+}$ complexes by 1-hydroxy-1-methylethyl radicals at 25 °C, $[H^+] = 0.01$ M, and $\mu = 0.1$ M ($HClO_4$ + $LiClO_4$) in 1 M 2-propanol.

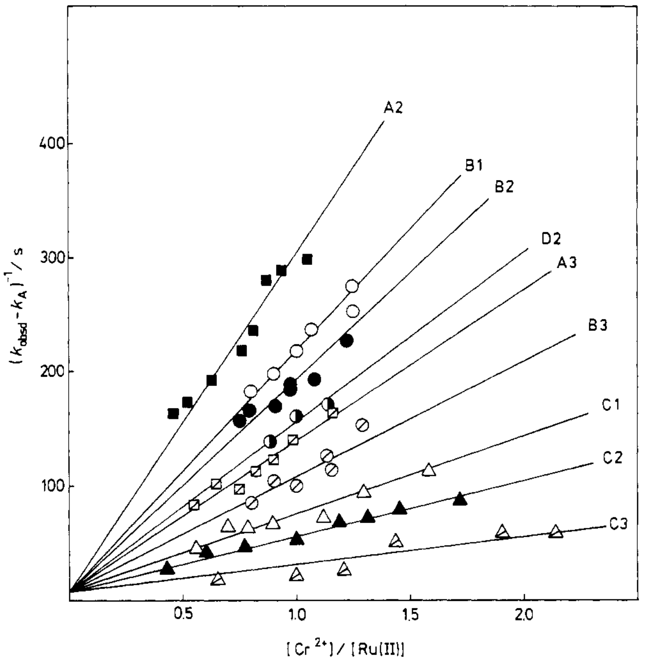

Figure 2. Acidity dependence of the plots of $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[Ru(II)]$ for the oxidation of ruthenium(II) complexes by 1-hydroxy-1-methylethyl radicals at 25 °C and $\mu = 0.1$ M in aqueous 1 M 2-propanol: (A) $(NH_3)_5Ru(3\text{-}Cl\text{-}py)^{2+}$; (B) $(NH_3)_5Ru(py)^{2+}$; (C) $Ru(NH_3)_6^{2+}$; (D) $(ND_3)_5Ru(py)^{2+}$. Acid concentrations are as follows: (1) 0.003 M H^+; (2) 0.01 M H^+; (3) 0.1 M H^+.

shown in Table II together with the ranges of the reactant concentrations used. The slopes are composite values representing $k_{Cr}/k_R k_H$. The values $k_H = 0.127$ s^{-1} [19] and $k_{Cr} = 5.1 \times 10^7$ M^{-1} s^{-1} [22] were used to calculate k_R, the second-order rate constants for the reactions between 1-hydroxy-1-methylethyl radicals and the ruthenium(II) complexes. The values of k_R so obtained are given in Table III.

Variation of $[H_3O^+]$. The dependence of k_R on acidity was tested for four of the ruthenium(II) complexes. At different but constant acidities different straight lines are obtained upon plotting $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[Ru(II)]$, as seen in Figure 2. Corresponding slopes are given in Table III. All of the values of k_R increase with increasing $[H^+]$, well outside the experimental error. Typically, this amounts to a factor of about 3 over the range 0.01–0.1 M, the upper limit being set by the ionic strength of 0.1 M chosen for this investigation. Since neither k_H nor k_{Cr} varies with $[H^+]$ over this range of acidities, the acidity dependence of the slopes as given in Table III can properly be ascribed to k_R. Such a variation of the rate constant with $[H^+]$ at acidic pH (note that the pK_a value of the radical is 10.8) is unprecedented in the earlier work; the *reductions* of species such as $(NH_3)_5Co(NC_5H_4X)^{3+}$ and $(H_2O)_5Cr(NC_5H_4X)^{3+}$ with this radical are independent of $[H^+]$,[10,11] as are the *oxidations* of Eu^{2+}(aq) and $V(H_2O)_6^{2+}$.[24,25]

Table II. Ranges of the Concentrations Used and the Slopes of $(k_{obsd} - k_A)^{-1}$ versus $[Cr^{2+}]/[Ru(II)]$ Plots Obtained for the Oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ Complexes by 1-Hydroxy-1-methylethyl Radicals[a]

X	$[H^+]$/ M	$10^4 \times$ $[Cr^{2+}]$/ M	$10^4 \times$ [Ru(II)]/ M	$[Cr^{2+}]$/ [Ru(II)]	slope/s[b]
3-Cl	0.1	1.5–1.9	2–2.7	0.55–1.2	131 ± 3
	0.01	1.4–2.2	1.9–3.0	0.46–1.1	295 ± 7
	0.01	1.4–2.5	1.8–3.0	0.35–1.0	340 ± 5[c]
H	0.1	1.7–2.4	1.9–2.2	0.8–1.3	101 ± 4
	0.01	1.7–2.5	1.9–2.5	0.7–1.3	178 ± 5
	0.01	1.7–2.0	1.7–2.0	0.8–1.15	146 ± 3[d]
	0.003	1.6–2.4	1.9–2.0	0.8–1.25	204 ± 5
4-CH$_3$	0.01	1.4–2.4	1.9–2.2	0.68–1.35	169 ± 5
4-C(CH$_3$)$_3$	0.01	1.4–2.4	1.7–2.0	0.73–1.2	148 ± 3
4-N(CH$_3$)$_2$	0.0002	1.1–1.8	0.9–1.5	1.22–2.4	72 ± 4
Ru(NH$_3$)$_6^{2+}$[e]	0.1	2.0–5.0	2.3–3	0.65–2.15	20.1 ± 2.8
	0.01	2.0–5.0	2.0–5.0	0.43–2.1	49 ± 2
	0.03	2.0–6.0	2.0–5.0	0.56–1.6	65 ± 2

[a] Conditions: 25 °C; $\mu = 0.1$ M ($LiClO_4$ + $HClO_4$) in aqueous 1 M 2-propanol. [b] Uncertainties quoted are standard deviations. [c] $\mu = 1.0$ M. [d] Ru(II) = $(ND_3)_5Ru(NC_5H_5)^{2+}$. [e] $Ru(NH_3)_6^{2+}$ instead of $(NH_3)_5Ru(NC_5H_4X)^{2+}$.

Table III. Rate Constants of the Oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ by 1-Hydroxy-1-methylethyl Radicals and $Co(bpy)_3^{3+}$[a]

X	$[H^+]$/M	$10^{-6}k_R$/ M^{-1} s^{-1}	$10^{-2}k_{Co}$/ M^{-1} s^{-1}	σ[b]
3-Cl	0.10	3.1	...	+0.37
	0.01	1.35	1.5	
	0.01	1.2[c]	...	
H	0.10	4.0	4.53	0
	0.01	2.25	4.5	
	0.01	2.75[d]	...	
	0.003	1.95	...	
4-CH$_3$	0.01	2.4	10	−0.17
4-C(CH$_3$)$_3$	0.01	2.7	11.3	−0.20
4-N(CH$_3$)$_2$	0.0002	5.6	288	−0.83
Ru(NH$_3$)$_6^{2+}$[e]	0.10	20	115	...
	0.01	8.2	113	
	0.003	6.2	105	
	10^{-8}	...	110[f]	

[a] Conditions: 25 °C; $\mu = 0.1$ M $HClO_4$ + $LiClO_4$ in aqueous 1 M 2-propanol. [b] Hammett σ values. [c] $\mu = 1.0$ M. [d] Ru(II) = $(ND_3)_5Ru(NC_5H_5)^{2+}$. [e] $Ru(NH_3)_6^{2+}$ instead of $(NH_3)_5Ru(NC_5H_4X)^{2+}$. [f] In 0.1 M NaCl.[26]

Table IV. Rate Constants for the Acid-Independent and Acid-Catalyzed Paths for the Oxidation of Ruthenium(II) Complexes by 1-Hydroxy-1-methylethyl Radicals[a]

	$(NH_3)_5Ru(3\text{-}Cl\text{-}py)^{2+}$	$(NH_3)_5Ru(py)^{2+}$	$Ru(NH_3)_6^{2+}$
k_{R0}/M^{-1} s^{-1}	1.1×10^6	1.9×10^6	6.3×10^6
k_{R1}/M^{-2} s^{-1}	1.95×10^7	2.05×10^7	1.35×10^8

[a] Conditions: 25 °C and $\mu = 0.1$ M in aqueous 1 M 2-propanol.

The oxidation of these ruthenium(II) complexes is thus acid-catalyzed, with the second-order rate constant k_R linearly dependent on $[H^+]$. The specific rates for the acid-independent and

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acid-dependent terms, designated k_{R0} and k_{R1} in eq 10, are given in Table IV.

$$k_R = k_{R0} + k_{R1}[H^+] \tag{10}$$

Since the acidity dependence was observed for the reaction of 1-hydroxy-1-methylethyl radicals with $Ru(NH_3)_6^{2+}$, the fastest reacting ruthenium(II) complex, and with the less reactive species $(NH_3)_5Ru(py)^{2+}$ and $(NH_3)_5Ru(3\text{-Cl-py})^{2+}$, it can be inferred that the other ruthenium(II) complexes studied, investigated only at 10^{-2} M H^+, behave similarly.

Other Variations. Kinetic runs for all ruthenium(II) complexes studied were performed at 0.1 M ionic strength (adjusted with $LiClO_4$) because at $\mu = 1$ M the solubility of some Ru(II) complexes was inconveniently reduced. Only for $(NH_3)_5Ru(3\text{-Cl-py})^{2+}$ was the rate also determined at $\mu = 1$ M; a minimal but seemingly real ionic strength effect was noted (Table III). To check the calculations of $(k_{obsd} - k_A)^{-1}$ values, several blank runs of spontaneous acidolysis (eq 3) were done at 0.1 M ionic strength. These gave values similar to those at $\mu = 1$ M, within experimental error.

Kinetic experiments probing for a deuterium effect were done by using $(ND_3)_5Ru(py)^{2+}$ in H_2O. A small effect, $k_D/k_H = 1.2$, was observed (Table III).

Oxidation of Ruthenium(II) Complexes by $Co(bpy)_3^{3+}$. For the purpose of comparison with the reactions of the radical, the reactions between the same series of Ru(II) complexes and $Co(bpy)_3^{3+}$ were briefly investigated. The kinetics of oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ were measured for each Ru(II) complex at several different concentrations of Co(III), which was in high excess over [Ru(II)].

Good pseudo-first-order kinetics were obtained according to $k_{obsd} = k_{Co}[Co(III)]$. The second-order rate constants k_{Co} are listed in Table III. The kinetics of oxidation of $Ru(NH_3)_6^{2+}$ by $Co(bpy)_3^{3+}$ were checked in the range of 0.1–0.001 M acidity and $\mu = 0.1$ M, with different concentrations of Ru(II) used in high excess over the concentration of Co(III). The runs were conducted at 285 nm, where interferences of the subsequent aquations of the $Co(bpy)_3^{2+}$ product are successfully avoided. No acidity dependence of the second-order rate constant was observed, and the same value was obtained as previously[26] at pH 8, as indicated in Table III.

Interpretation and Discussion

The kinetic data (for the part of the reaction other than the nonproductive acidolysis "background") are characterized by a direct dependence on the concentration of the ruthenium(II) complex and by an inverse dependence on the chromium(II) concentration. These dependences are the experimental facts that are established by the linearity of the plots given in Figures 1 and 2. The algebraic forms are those expected from the two competitive reactions of the radical implied, capture by chromium(II) versus reaction with ruthenium(II).

As presented earlier, this means that the rate constants k_R determined from the slopes of these plots represent, directly or indirectly, the reaction in which the metal complex is oxidized by this radical. As we shall see, however, the experimental rate constant k_R is not simply k_5, in part because this is influenced by the fate of the Ru(III) complex formed in eq 5 and in part because the hydrogen ion dependence signals that the reaction given by eq 5 is not a single-step, elementary reaction.

Fate of Ruthenium(III). Reactions 6 and 7 are independently known.[5,23] Were reaction 7 not important, then regardless of whether reaction 6 occurred or not, the equality $k_5 = k_R$ would apply.

This is not the case, however, since $^{\bullet}C(CH_3)_2OH$ rapidly reduces such Ru(III) complexes. For example, $(NH_3)_5RuCl^{2+}$ reacts with $k_7 = 1 \times 10^9$ M^{-1} s^{-1},[5] and the others almost certainly have comparable values. Were reaction 7 important, but not reaction 6, then the set of relevant reactions would consist of eq 4, 5, and 7. In that case the relationship between the rate constants would be the simple one $k_R = 2k_5$. The net chemical reaction should be disproportionation of the aliphatic radical, as (weakly) catalyzed by ruthenium(II). The catalytic sequence avoids any radical–radical self-reaction. That is, ruthenium(III) would not accumulate (as observed), and the organochromium(2+) cation would be lost by the net reaction of eq 11, a process of stoichiometric

$$2CrC(CH_3)_2OH^{2+} = 2Cr^{2+} + (CH_3)_2CO + (CH_3)_2CHOH \tag{11}$$

but not mechanistic significance. This situation comes the closest to being realized for $Ru(NH_3)_6^{3+}$, which reacts with Cr^{2+} relatively slowly;[27] $k_6 = 28$ M^{-1} s^{-1}.

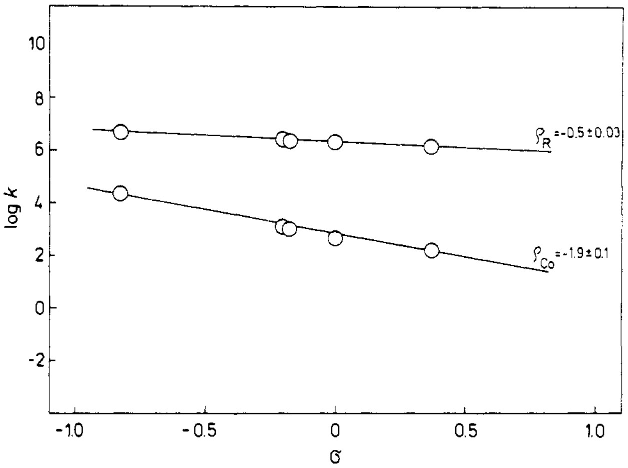

Figure 3. Plots of the logarithms of the rate constants for the oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ complexes by 1-hydroxy-1-methylethyl radicals (k_R) and by $Co(bpy)_3^{3+}$ (k_{Co}) versus the Hammett σ values for the substituents X of the coordinated pyridine ligand. The rate constants decrease in both series in the order X = $4\text{-N(CH}_3)_2 > 4\text{-C(CH}_3)_3 > 4\text{-CH}_3 > H > 3\text{-Cl}$. The rate constants k_R are the values obtained at the lower limit of [H^+] studied (Table III).

The reactions of the pyridine-containing ruthenium(III) complexes with chromium(II) occur more rapidly; the parent complex $(NH_3)_5Ru(py)^{3+}$ has $k_6 = 3.4 \times 10^3$ M^{-1} s^{-1}.[23] This is sufficiently rapid in comparison with eq 7 that both occur competitively over the course of the reaction. It is an uneven competition, however, since in reaction 6 the reagent, Cr^{2+}, remains at essentially constant concentration, whereas in reaction 7 the value of [$^{\bullet}C(CH_3)_2OH$] is small but time-dependent.

To assess how important this competition is, it was necessary to treat the full kinetic scheme, including acidolysis (eq 3) and all of the ruthenium-related reactions (eq 4–7). These equations do not have a closed-form solution under the conditions used. A numerical solution, obtained by use of the program KINSIM,[28] confirmed the qualitative situation described. In summary, these simulations showed that k_R will lie between k_5 and $2k_5$. With the rate constants given, at typical concentration of the reagents, $k_R \approx 1.3k_5$. The effect is small enough that we shall neglect it in the subsequent discussion and consider the chemical significance of k_R values as if they did represent k_5 exactly. We are satisfied that this approximation can be made without great distortion because k_R is so little dependent upon different variables. Needless to say, the rate constants for the simple electron-transfer reactions between the Ru(II) complexes and $Co(bpy)_3^{3+}$ are not complicated by any such considerations.

Substituent Effects. Both sets of rate constants for the Ru(II) substituted-pyridine complexes are closely correlated by the Hammett equation. Figure 3 depicts this result and gives the reaction constants (ρ) −0.50 ± 0.03 and −1.9 ± 0.1 for the reactions of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ with $^{\bullet}C(CH_3)_2OH$ and $Co(bpy)_3^{3+}$, respectively.

These negative values of ρ contrast with the positive ones found for every reaction in which the radical acts as an oxidizing

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[26] Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

[27] Endicott, J. F.; Taube, H. *Inorg. Chem.* **1965**, *4*, 437.

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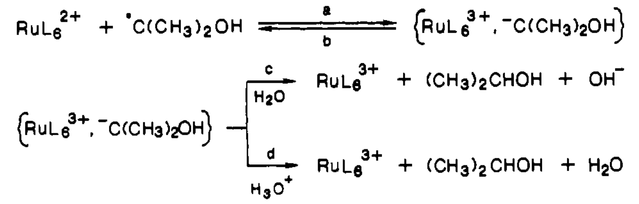
Scheme I



agent.[9-11] Since the electron transfers in opposite senses, opposite inductive effects are to be expected. Also, the value of the reaction constant is "small", just as it is in those reactions in which the radical or other electron donors react with pyridine-containing substrates, provided the pyridine itself is not intimately involved.[9-11] This allows us to argue that the pyridine ligands in reaction 5 play no role other than to exert weak inductive effects consistent with the direction of electron transfer. Both rate constants k_R and k_{Co} for $(NH_3)_5Ru(4\text{-}N(CH_3)_2\text{-}py)^{2+}$ fit very well on the lines in Figure 3 defined by the other four complexes. This may be taken as evidence that the value of σ_p used, −0.86, is the correct one and that the nitrogen of the dimethylamino group is not protonated at 2×10^{-4} M H^+. If σ_p for the $HN(CH_3)_2^+$ group is used ($\sigma_p > 1$), the fit in Figure 3 becomes much less satisfactory.[29]

Effect of [H⁺]. The reaction between $\cdot C(CH_3)_2OH$ and the ruthenium(II) complexes is the only acid-accelerated reaction of this radical that has been reported. This aspect is central in assessing the mechanism that follows. We discard at the outset a simple electron-transfer process leading directly to the separated ions RuL_6^{3+} and R^-, on the thermodynamic grounds cited earlier, and also on the basis that the proton acceleration is not thereby explained. The barely appreciable kinetic isotope effect for $(ND_3)_5Ru(py)^{2+}$ (k_D/k_H = 1.2, Table III) as compared to that for $(NH_3)_5Ru(py)^{2+}$ in H_2O leads us also to discount a mechanism in which a hydrogen atom is abstracted from an ammine ligand.

The most probable formulation is an electron-transfer reaction within a precursor complex formed by association of the radical with the ruthenium(II) complex. That yields an ion pair, $\{RuL_6^{3+}, ^-C(CH_3)_2OH\}$, which could then be solvolyzed by H_2O or H_3O^+ competitively with its return to reactants. This is represented in Scheme I.

This scheme leads to an equation that has the required algebraic form, provided (as expected) that the electron-transfer step occurs rapidly and reversibly as compared to the solvolysis reactions. In that case the apparent rate constant k_R is given by eq 12.

$$k_R = (k_a k_c/k_b) + (k_a k_d/k_b)[H^+] \qquad (12)$$

The rate constants k_{R0} ($=k_a k_c/k_b$ in this model) were the ones that were considered in light of the substituent constants, since it was at pH ≥2 that evaluations were made for all of the substituted species. The solvolytic term k_c will be negligibly influenced by substituent, and substituent effects on k_a and k_b are evidently quite small.

The rate constants for the oxidations of RuL_6^{2+} by $\cdot C(CH_3)_2OH$ and by $Co(bpy)_3^{3+}$ correlate well with one another. Figure 4 depicts a plot of log k_R versus log k_{Co}. As indicated, the point for $Ru(NH_3)_6^{2+}$ lies along the same line. This also supports the mechanism shown in Scheme I, since the initial step is electron transfer.

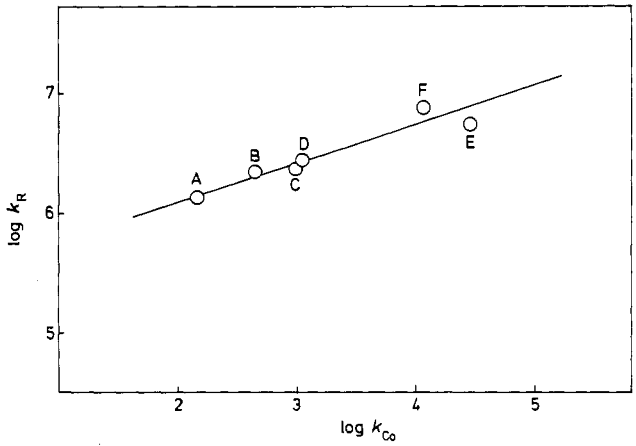


Figure 4. Plots of the logarithms of the rate constants for the oxidation of $(NH_3)_5Ru(NC_5H_4X)^{2+}$ and $Ru(NH_3)_6^{2+}$ complexes by 1-hydroxy-1-methylethyl radicals (k_R) versus log k_{Co} for the oxidation of the same complexes by $Co(bpy)_3^{3+}$ ions at 25 °C, $[H^+]$ = 0.01 M, and μ = 0.1 M ($HClO_4$ + $LiClO_4$). The pyridine substituents X are as follows: (A) 3-Cl; (B) H; (C) 4-CH_3; (D) 4-$C(CH_3)_3$; (E) 4-$N(CH_3)_2$. (F) refers to $Ru(NH_3)_6^{2+}$.

It should be noted that in this proposal the unanticipated acid acceleration is caused by the intervention of an acid-promoted term in the solvolysis. This seems reasonable, since the acidolyses of metal–carbon bonds in protic media do, in general, reflect contributions from all sources of protons, free H_3O^+ as well as water molecules in the secondary coordination sphere of the ruthenium complex.

The acid catalysis, unique to the Ru(II) oxidations, might instead arise from protonation of the filled metal t_{2g} orbitals. The species so suggested, also unique to Ru(II), is responsible for the remarkable and otherwise anomalous acid catalysis of aquation reactions of species such as $Ru(NH_3)_6^{2+}$ and $(NH_3)_5Ru(py)^{2+}$.[30] This suggestion is embodied in eq 13 and 14.

$$RuL_6^{2+} + H^+ \rightleftharpoons L_6RuH^{3+} \quad K_{13} \qquad (13)$$

$$L_6RuH^{3+} + \cdot C(CH_3)_2OH \rightarrow RuL_6^{3+} + (CH_3)_2CHOH \quad k_{14} \qquad (14)$$

We find this possibility less attractive than that shown in Scheme I for several reasons. First, it should then be only coincidence that causes the relative importance of k_{R0} and k_{R1} (here, $k_{R1} = K_{13}k_{14}$) to be nearly the same for the three Ru(II) complexes studied. Second, it would require a different pathway for the acid-independent term, and thus steps in Scheme I, other than the k_d step, would need to be retained. In that event it is difficult to understand why the solvolysis steps utilize solvent alone (k_c). Third, there is little indication that the protonation is very prevalent at 0.1 M H^+. For rate constants as large as k_{R1} ($\sim 10^7$ M^{-1} s^{-1}, Table IV), a small value of K_{13} would require k_{14} at or near the diffusion-controlled limit. In no other case, however, has a proton-assisted electron-transfer reaction of these Ru(II) complexes been noted. We thus think it more likely that the proton is involved in the solvolytic steps, as in Scheme I.

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(29) We are grateful to a reviewer for bringing this point to our attention.

(30) Ford, P. C.; Kuempel, J. R.; Taube, H. *Inorg. Chem.* **1968**, 7, 1976.