evidence, the latter seems the more conservative interpretation.

There is a second transient species seen at 4 ppm in the ^{31}P NMR spectrum shown in Figure 5A. Because this feature disappears in the spectrum of the principal intermediate recorded at −80 °C and is also absent in the reaction product, we suggest that it can be attributed to a second intermediate. There is no real proof of this assignment and certainly no suggestion as to what its structure and composition might be, but the kinetic and spectrophotometric complications that appear at $[SO_2] > 0.2$ M lend credence to this suggestion. Whatever its role, it is clearly a species not important under the conditions used in most of the experiments reported herein.

Oxidation of $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$. It has been shown that S_7 can be smoothly converted to S_7O by using CF_3CO_3H[25] and that $Pd_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$ can be converted to $Pd_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$ by using m-chloroperoxybenzoic acid.[32] Experiments were conducted with $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$ by mixing the reagents at −30 °C in CD_2Cl_2 and recording the ^{31}P NMR spectra at −20 °C. When the amount of MCPBA was stoichiometric or less, $Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2$ was indeed the major product, although small amounts of unidentified oxidation products were seen. With excess MCPBA, the μ-SO_2 A-frame was absent, and only oxidation products were found.

Conclusions. The principal findings of the work can be summarized as follows. The insertion of sulfur dioxide into the Pt–Pt bond yields an A-frame known to have a structure in which the sulfur atom is bound to both platinums with equivalent and noncoordinated oxygen atoms. This reaction proceeds by way of an intermediate readily observed and characterized in a consistent manner by both spectroscopy and kinetics. The structure of the intermediate cannot be defined unambiguously but is most probably a loosely bound charge-transfer complex.

A single S atom from S_8 inserts into the Pt–Pt bond. The reaction is able to utilize all or nearly all of the sulfur atoms of the reactant under suitable reaction conditions. The rate of this reaction, like that of diazomethane, is strongly dependent on the terminal ligands bound to the metal. In both cases the rate is much lower when halides are replaced by uncharged Lewis bases (CO, py, NH_3). (In qualitative experiments, the same was found for sulfur dioxide insertion). Clearly, then, the mechanism is not nucleophilic attack of the inserting reagent on the metal center, a process that would be accelerated by increased positive charge at the attack site. These data suggest that cleavage of the Pt–Pt bond occurs during the activation step, not subsequent to it. The rate constants for both reactions are characterized by sizable activation enthalpies, 15.1 and 22.2 kcal/mol, for S_8 and SO_2, respectively. That, too, speaks to compensating bond making and bond breaking in the activated complex, since (for example) the former value is considerably low than the S–S bond energy.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82. The Nicolet NT-300 NMR spectrometer was purchased in part with funds from a grant from the National Science Foundation (No. CHE-3209709) to the Department of Chemistry at Iowa State University.

Registry No. S_8, 10544-50-0; SO_2, 7446-09-5; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2Br_2(\mu\text{-dppm})_2$, 61250-66-6; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4; $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$, 64387-53-7; $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$, 68851-45-6; $[Pt_2(NC_5H_5)_2(\mu\text{-dppm})_2]^{2+}$, 68851-56-9; $[Pt_2(NH_3)_2(\mu\text{-dppm})_2]^{2+}$, 68851-54-7; $Pt_2Br_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 102494-78-0; $Pt_2I_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 102494-79-1; $Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2$, 68851-48-9.

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Kinetics of Reduction of a Series of Pentaaquo(pyridine)chromium(III) Ions by 1-Hydroxy-1-methylethyl Radicals: Evidence for Electron Transfer to Pyridine

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The title reaction was investigated for a series of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ ions. The rate constants are correlated by the Hammett equation. These data, in comparison to other cases in the literature, provide support for a mechanism in which a pyridyl radical, coordinated to Cr(III), is first formed. Subsequent intramolecular electron transfer to produce Cr^{2+} and pyH^+ occurs more rapidly. Additional members of the series of free pyridinium ions, $C_5H_4XNH^+$, were also investigated.

Introduction

A question of continuing interest to us[1] and others[2-9] concerns the site of electron transfer in transition-metal complexes. At issue for any given family of outer-sphere reactions is whether the reaction occurs via prior ligand reduction ("chemical mechanism") or directly at the metal center ("resonance transfer").[10] The issue is particularly pertinent when one or more ligands is known independently to be redox active,[2] such as a phenanthroline[3] or a pyridine,[1,11] and when the reaction has a large thermodynamic driving force. The latter is the case for $^{\bullet}C(CH_3)_2OH$, a powerful reductant ($E^\circ \sim -1.3$ V), and for alkyl radicals,[3] which are strong oxidants. A method for deciding the mechanism in a specific case or in general, is not readily at hand. Product analysis, for example, is not definitive since additional reactions often occur immediately after the initial step.

We recently suggested[1,11] that a helpful approach in certain instances can be based on a linear free energy relationship (LFER). Applied to reactions of $(NH_3)_5Co(py)^{3+}$ (where py = NC_5H_5 and

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Table I. Visible Absorption Maxima of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ Ions

X	λ_{max}/nm ($\epsilon/M^{-1}\ cm^{-1}$)		
4-CN[a]	560 (18.1)	402 (20.4)	278 (3.28×10^3)
3-CN[b]	560 (19.0)	402 (20.5)	271 (2.90×10^3), 265 (3.38×10^3)
3-Cl[b]	560 (18.5)	402 (20.6)	273 (3.43×10^3)
4-Cl[a]	558 (19.0)	400 (21.0)	258 (3.30×10^3)
H[c]	560 (18.2)	402 (20.8)	260 (3.46×10^3)
4-*tert*-butyl[a]	558 (18.5)	400 (21.3)	256 (2.90×10^3)

[a] This work. [b] Reference 14. [c] Reference 13.

analogues substituted in the 3- and 4-positions), this method allowed us to conclude that Co(II) was formed directly, not via intramolecular electron transfer.[11] The reductions of pyridinium ions (pyH^+ and $pyCH_3^+$) by $^{\bullet}C(CH_3)_2OH$,[12] where no other reducible center is present, show different characteristics, consistent with (and, we would assert, indicative of) the necessarily different mechanism.

We report here data for a different reaction series, $(H_2O)_5Cr(NC_5H_4X)^{3+}$ (X = H, 4-CN, 3-CN, 4-Cl, 3-Cl, 4-*t*-Bu) (eq 1). Because the Cr(III) is kinetically difficult but not impossible to reduce, it is not easy to anticipate the mechanism. This system becomes, then, a critical test of the applicability of the LFER method suggested[1] to be useful in these cases. As a part of this investigation, additional free-substituted pyridinium ions were examined (eq 2) to facilitate comparisons between the systems.

$$(H_2O)_5Cr(NC_5H_4X)^{3+} + {}^{\bullet}C(CH_3)_2OH + H_2O = Cr(H_2O)_6^{2+} + (CH_3)_2CO + HNC_5H_4X^+ \quad (1)$$

$$XC_5H_4NH^+ + {}^{\bullet}C(CH_3)_2OH = XC_5H_4NH^{\bullet} + (CH_3)_2CO + H^+ \quad (2)$$

Experimental Section

Materials. The various Cr(III) complexes in acidic solution were prepared by the previously described method, which involves reduction of the corresponding pyridine adducts of diperoxychromium(VI) species with acidic iron(II) perchlorate followed by cation-exchange separation.[13,14] Their purity was checked by chromium analysis[15] and by qualitative and quantitative determination of the pyridine by UV spectrophotometry after aquation of the complex. In subsequent preparations their identities and concentrations were ascertained by the positions and molar absorptivities of the visible absorption maxima, as given in Table I.

Commercial pyridines were purified before use. 3-Chloro- (Merck) and 4-*tert*-butylpyridine (Fluka) were distilled at a reduced pressure, the latter several times successively. 4-Chloropyridine (Merck), obtained as the hydrochloride, was recrystallized from dilute perchloric acid, and the free base was extracted by diethyl ether. 3-Cyano-, 4-cyano-, and 4-(dimethylamino)pyridine were repeatedly recrystallized from water.

Lithium perchlorate, prepared by neutralizing lithium carbonate with perchloric acid (both Merck analytical grade), was recrytallized three times from water. All other chemicals used were analytical grade. Redistilled water was used throughout. Oxygen-sensitive materials were handled by syringe–septa methods under highly purified nitrogen, which was first passed over a heated copper catalyst and then through successive Cr^{2+} scrubbing towers.

The source of the aliphatic radical was the organochromium complex $(H_2O)_5CrC(CH_3)_2OH^{2+}$. It was prepared, as described in detail earlier,[1,12,16–20] by the reaction between $Cr(H_2O)_6^{2+}$ and H_2O_2 in aqueous perchloric acid solutions containing 2-propanol (eq 3). The alcohol was

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

distilled weekly or as needed, and was stored out of direct light to inhibit the formation of interfering peroxides.

Techniques. The reactions of $Cr(py)^{3+}$ and pyH^+ and their substituted analogues were monitored spectrophotometrically at an absorption maximum for $CrC(CH_3)_2OH^{2+}$ (λ = 311 nm, ϵ = 2500 $M^{-1}\ cm^{-1}$; λ = 407 nm, ϵ = 700 $M^{-1}\ cm^{-1}$),[21] as described previously.[1] The oxidant ($Cr(py)^{3+}$ or pyH^+) and Cr^{2+} were both present in kinetic runs at concentrations substantially higher than that of $CrC(CH_3)_2OH^{2+}$, so that both were nearly constant in a given experiment. In most instances (including all for which numerical data are reported) the reaction followed pseudo-first-order kinetics. Such data were analyzed by standard methods. That was not the case for two of the substituted pyridinium ions (3-CN and 4-CN), however, and complex kinetics were found. The complications did not arise from concentration conditions, however, but from the chemical reactions themselves, as detailed later.

The products from eq 1 were determined in one instance. The solution initially contained $CrC(CH_3)_2OH^{2+}$ (9.3×10^{-5} M), Cr^{2+} (4.6×10^{-5} M), and $Cr(NC_5H_4\text{-}3\text{-}Cl)^{3+}$ (2.1×10^{-4} M). After the reaction was complete, the Cr^{2+} was oxidized by $Co(NH_3)_5Cl^{2+}$, and Co^{2+} was determined by the thiocyanate method.[22] The pyridinium ion was identified by its characteristic UV spectrum after the chromium complexes were removed on a short column of cation-exchange resin.

Results

Reduction of Cr(III)–Pyridine Complexes by $^{\bullet}C(CH_3)_2OH$. Since the principles and practice of the method used for kinetics have been given before,[1,14–18] an abbreviated treatment suffices. The pertinent chemical equations are shown in eq 4–7, and the steady-state rate law is shown in eq 8.

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

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

$${}^{\bullet}C(CH_3)_2OH + (H_2O)_5Cr(py)^{3+} \rightarrow (H_2O)_5Cr(py)^{2+} + (CH_3)_2CO + H^+ \quad (k_R) \quad (6)$$

$$(H_2O)_5Cr(py)^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{2+} + pyH^+ \quad (7)$$

$$\frac{-d[CrR^{2+}]}{dt} = \left(k_A + \frac{k_H k_R[Cr(py)^{3+}]}{k_R[Cr(py)^{3+}] + k_{Cr}[Cr^{2+}]}\right)[CrR^{2+}] \quad (8)$$

Because $[Cr(py)^{3+}]_0$ and $[Cr^{2+}]_0$ were much higher than $[CrR^{2+}]_0$, a pseudo-first-order analysis was successively conducted in each case. For most complexes, the measured rate constants varied with reagent concentrations, as expected from eq 8. Table II presents the experimental rate constant for each of the compounds where measurements were completed, which includes substituents with X = 4-CN, 3-CN, 4-Cl, and 3-Cl.

In several instances, however, including the parent complex $(H_2O)_5Cr(NC_5H_5)^{3+}$, the rate constant remained invariant (at $k_{obsd} = k_A$, within experimental error), even in experiments with no added Cr^{2+}. That is also consistent with eq 8, provided $k_R[Cr(py)^{3+}] << k_{Cr}[Cr^{2+}]$. In other words, these members of the series react too slowly with $^{\bullet}C(CH_3)_2OH$ for successful kinetic measurements of k_R even under optimum conditions. The respective upper limits of k_R, $<5 \times 10^4$ and $<1 \times 10^5$ $M^{-1}\ s^{-1}$, were estimated for $(H_2O)_5Cr(NC_5H_5)^{3+}$ and $(H_2O)_5Cr(NC_5H_4\text{-}4\text{-}C(CH_3)_3)^{3+}$. A cursory examination of *cis*-$(H_2O)_4Cr(NC_5H_5)_2^{3+}$ yielded an approximate value for k_R of 1×10^5 $M^{-1}\ s^{-1}$.

The values of all rate constants in eq 8, other than k_R, are known from previous work, as follows. The acidolysis reaction has been studied independently;[1,16–21] the expression applicable is $k_A/s^{-1} = 3.31 \times 10^{-3} + (4.91 \times 10^{-3})[H^+]$ under these conditions. The

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Table II. Rate Constants Observed for the Reduction of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ Complexes and $HNC_5H_4X^+$ Ions by 1-Hydroxy-1-methylethyl Radicals at 25 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in 1 M Aqueous 2-Propanol[a]

X	$10^4[Cr^{2+}]$/ M	$10^4 \times [(H_2O)_5Cr(NC_5H_4X)^{3+}]$/M	10^3k_{obsd}/ s^{-1}	$10^4[Cr^{2+}]$/ M	$10^4 \times [(H_2O)_5Cr(NC_5H_4X)^{3+}]$/M	10^3k_{obsd}/ s^{-1}
4-CN	7.35	1.96	98	17.9	1.50	69.5[b]
	11.1	1.96	98	19.6	1.48	63
	11.9	1.98	81.5[b]	22.5	1.50	59[b]
	15.0	1.98	70[b]	23.9	1.59	51.5
	16.9	1.69	73.5	24.8	1.49	50[b]
	17.2	1.73	63[b]	24.8	1.49	49.5
	37.4	3.19	64	37.6	1.96	48
3-CN	1.14	2.09	116	5.73	2.09	78.5
	1.95	2.20	97.5	7.1	2.20	67
	2.91	2.20	95	8.0	2.09	65.5
	4.49	2.20	81.5	8.5	1.88	61.5
3-Cl	1.09	3.47	32.5	4.28	3.47	12.6
	1.67	2.94	24.1	4.44	3.08	10.6
	2.64	3.21	17.5	5.71	3.47	10.7
	3.09	3.47	15.7	7.02	3.47	9.2
	3.03	3.08	13.6	4.97	2.12	8.7
	2.24	2.14	14.8	6.23	2.31	8.0
	3.74	2.11	12.9			
4-Cl	0.95	3.50	7.7	3.23	3.50	5.35
	1.56	3.50	6.35	3.72	3.50	5.35
	1.99	3.50	5.8	3.67	3.50	4.9
	2.62	3.50	5.55	4.22	3.50	4.9
	2.79	3.50	4.75			

X	$10^4[Cr^{2+}]$/M	$10^4[HNC_5H_4X^+]$/M	$10^3k_{obsd}/s^{-1}$	$10^4[Cr^{2+}]$/M	$10^4[HNC_5H_4X^+]$/M	$10^3k_{obsd}/s^{-1}$
3-Cl	1.67	1.98	93.5	9.55	0.99	19.8
	9.55	4.0	52.5	19.6	1.64	16.9
	9.55	2.0	34.5	19.6	0.99	12.6
	19.6	2.68	26.0			
4-Cl	9.35	54.0	28.5	9.7	9.35	9.6
	10.2	33.7	21.5	9.6	7.54	9.0
	4.11	9.55	15.5	9.35	7.02	8.55
	10.2	13.4	11.5	9.6	6.33	8.25
	4.11	4.78	9.6			

[a] $[(H_2O)_5CrC(CH_3)_2OH^{2+}] \approx 2 \times 10^{-5}$ M; data are listed in increasing order of the ratio $[Cr^{2+}]/[Cr(py)^{3+}]$. [b] $[H^+] = 0.5$ M.

Table III. Kinetic Data for the Reduction of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ Complexes by 1-Hydroxy-1-methylethyl Radicals at 25 °C, $[H^+] = 0.1$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in 1 M Aqueous 2-Propanol

X	slope/s[a,b]	$k_R/M^{-1}\ s^{-1}$
4-CN	0.765 ± 0.026	5.3×10^8
3-CN	2.22 ± 0.08	1.8×10^8
3-Cl	85.6 ± 1.5	4.7×10^6
4-Cl	789 ± 26	5.1×10^5
py_2[c]		$\sim 10^5$
H		$<5 \times 10^4$[d] (1.1×10^4)[e]
4-*tert*-butyl		$<1 \times 10^5$[d] (4.4×10^2)[e]

[a] Uncertainties quoted are standard deviations. [b] The slope of plots of $1/\Delta k$ vs. $[Cr^{2+}]/[Cr(III)]$. [c] Complex is *cis*-$(H_2O)_4Cr(NC_5H_5)_2^{3+}$. [d] Estimated by assuming that a half-life 10% different from that for acidolysis would have been noticed. [e] Calculated from eq 13 by using corresponding Hammett σ values.

homolysis reaction, eq 5, is characterized by forward[17] and reverse[21] rate constants $k_H = 0.127\ s^{-1}$ and $k_{Cr} = 5.1 \times 10^7\ M^{-1}\ s^{-1}$. Least-squares analysis of the values of k_{obsd} as a function of concentrations according to eq 8 affords the composite term k_{Cr}/k_Hk_R, which is designated *S*. The quantity *S* is the slope of a plot of $1/(k_{obsd} - k_A)$ vs. $[Cr^{2+}]/[Cr(py)^{3+}]$, which is the relationship illustrated in Figure 1. The values of *S* and of k_R calculated from it are shown in Table III for each complex investigated. The same table presents estimated limits for those members of the series that react too slowly to be evaluated.

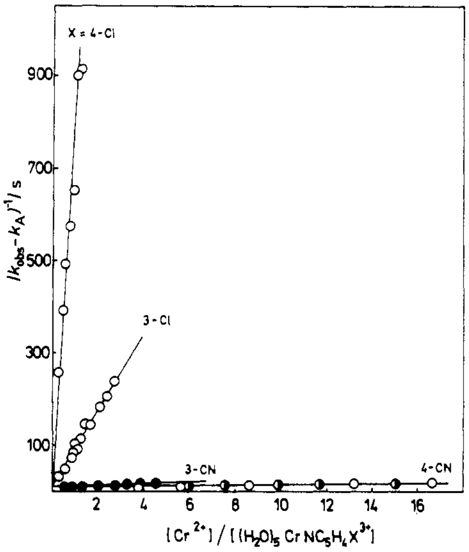

Figure 1. Plots of $(k_{obsd} - k_A)^{-1}$ vs. $[Cr^{2+}]/[Cr^{III}]$ for the reduction of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ complexes by 1-hydroxy-1-methylethyl radicals at 25 °C, $[H^+] = 0.100$ M, and $\mu = 1.0$ M ($HClO_4 + LiClO_4$) in aqueous 1 M 2-propanol. The substituents X are indicated in the figure. For X = 4-CN the points symbolized as ◑ refer to $[H^+] = 0.5$ M.

$Cr(NC_5H_4X)^{3+}$ and $^{\bullet}C(CH_3)_2OH$: Products and Stoichiometry. The methods described earlier were used to identify the products for the case $[CrNC_5H_4\text{-}3\text{-}Cl]^{3+}$. Cr^{2+} was identified on the basis of its reducing strength, and the substituted pyridinium ion was identified by its UV spectrum. The expected yield of each product is *not* the same as the value of $[CrR^{2+}]_0$, however, since a variable but often substantial proportion of the latter is "wasted" in the acidolysis reaction. Furthermore, the reaction (eq 2) between $^{\bullet}C(CH_3)_2OH$ and $3\text{-}Cl\text{-}C_5H_4NH^+$ (liberated in eq 1) will diminish the yields of the products. The amount of Cr^{2+} found, 78% of that expected,[23,24] is therefore considered in satisfactory agreement

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[23] The calculated yields were obtained from a numerical solution to the family of differential equations. The rate constants used were those determined here and previously. This solution used the program KINSIM,[24] generously supplied by Drs. B. L. Barshop and C J. Frieden.

with eq 1. The pyridinium ion produced was detected by its characteristic UV spectrum, but a quantitative analysis was not successful since it was not possible to allow for the unknown contribution of the dihydro-3-chloropyridine.

Reduction of Pyridinium Ions by $^{\bullet}C(CH_3)_2OH$. Several of these reactions had already been investigated.[12] We chose to extend the measurements to include additional substituents to allow better comparisons. The rate-limiting step is shown in eq 9, which is then followed by the disproportionation of the pyridyl radicals (eq 10). This treatment afforded the following values: for

$$pyH^+ + {}^{\bullet}C(CH_3)_2OH \rightarrow pyH^{\bullet} + (CH_3)_2CO + H^+ \quad (9)$$

$$2pyH^{\bullet} + H^+ \rightarrow pyH^+ + C_5H_6NH \quad (10)$$

$4\text{-}ClC_5H_4NH^+$, $S = 154 \pm 4$ s and $k_R = 2.6 \times 10^6\ M^{-1}\ s^{-1}$; for $3\text{-}ClC_5H_4NH^+$, $S = 5.4 \pm 0.1$ s and $k_R = 7.4 \times 10^7\ M^{-1}\ s^{-1}$.

Attempts to evaluate the kinetics for additional compounds, although unsuccessful numerically, proved instructive. Compounds with strongly electron-donating substituents (4-*tert*-butyl and $4\text{-}NMe_2$ were used) gave values of k_R that decreased with successive recrystallizations. We are not confident that the true limit was reached, however, and hence report no values for these two. This problem is not unexpected; very small values of k_R are consistent with the previously noted strong sensitivity of the k_R values for pyridinium ions to the ring substituent.[12] As such, accurate determinations of k_R require high values of the concentration ratio $[pyH^+]/[Cr^{2+}]$, as can be seen from eq 8. Trace impurities in the pyridinium salt would be most troublesome at high $[pyH^+]$.

Another pair of pyridinium ions (X = 4-CN and 3-CN) also gave difficulties not unlike those encountered previously[12] for nicotinamide. That is, additional spectral bands and/or reactions of the pyridyl radical with CrR^{2+} caused nonlinear first-order kinetic plots. These cases were not considered further.

Reactions between $Cr(NC_5H_4X)^{3+}$ and $V(H_2O)_6{}^{2+}$. Experiments were conducted for two complexes (X = 4-Cl and 4-CN) to explore the feasibility of an additional electron-transfer series. This would amount, in effect, to a V(II)-catalyzed aquation of $Cr(py)^{3+}$ via the sequence in eq 11 and 12 written by analogy to the known sequence[25] for $CrCl^{2+}$.

$$Cr(py)^{3+} + V^{2+} \xrightarrow{H^+} Cr^{2+} + V^{3+} + pyH^+ \quad (11)$$

$$Cr^{2+} + V^{3+} \rightarrow Cr^{3+} + V^{2+} \quad (12)$$

In one case (X = 4-Cl) the experiment failed because the rate was too low, and no change in $[Cr(py)^{3+}]$ was observed. In the other (X = 4-CN) the reaction was strongly autocatalytic, reminiscent of the electron-transfer chains noted by Gould et al.[26] The latter precluded a ready determination of k_{11} in this case as well, although it points to a phenomenon worthy of further investigation.

Discussion

The form of the kinetic equations shows that this aliphatic radical reacts directly with the $Cr(py)^{3+}$ complexes in a second-order and presumably bimolecular process. The observed production of Cr^{2+} and pyH^+ is consistent with aquation of a Cr(II)–pyridine complex, an expected intermediate whether derived directly by electron transfer or indirectly via unimolecular electron transfer within a complex consisting of a pyridyl radical bound to Cr(III).

The trend in k_R values between pyH^+ and $Cr(py)^{3+}$ values is relatively uniform, the former being some 5–30 times more reactive. On the other hand, some sharp contrasts are seen in comparing either of these with $Co(NH_3)_5py^{3+}$.[1] To cite specific examples, for X = 3-CN, $k_{R(Co)} < k_{R(Cr)}$ (by a factor of 1.3), whereas for X = 3-Cl the reverse order is found by a factor of 7, and for X = H and CH_3 the (extrapolated) rate ratios are even more in favor of cobalt (by $\sim 10^3$ and 10^4). This rate reversal is one of the factors indicating a change in mechanism.

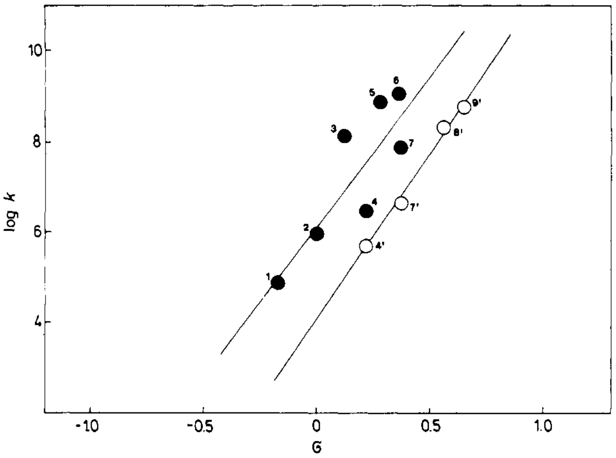

Figure 2. Plots of the logarithm of the rate constants for the reduction of $(H_2O)_5Cr(NC_5H_4X)^{3+}$ complexes (○) and $NC_5H_4XH^+$ ions (●) by 1-hydroxy-1-methylethyl radicals vs. the Hammett σ values for the substituents X, where X = $4\text{-}C(CH_3)_3$ (1), H (2), 3-OH (3), 4-Cl (4 and 4′), $3\text{-}CONH_2$ (5), $4\text{-}CONH_2$ (6), 3-Cl (7 and 7′), 3-CN (8′), and 4-CN (9′).

Substituent Effects. The reaction rates for the series of $Cr(py)^{3+}$ complexes change quite markedly along the series of compounds investigated. The measured rate constants span a factor of $>10^2$, and if the case where only lower limits were set are also considered (X = H and CH_3), the range rises to $>10^3$. The trend in rate among the substituents found for $Cr(py)^{3+}$ is in the same direction as for pyH^+ and $(NH_3)_5Co(py)^+$. Not surprisingly, electron-withdrawing subsituents enhance the reactivity of all of these species as electron acceptors.

The greatly enhanced sensitivity of $Cr(py)^{3+}$ as compared to the $(NH_3)_5Co(py)^{3+}$ analogues is *not*, however, simply a matter that the less *reactive* substrates show greater *selectivity*. In fact, the complexes with the most electron-attracting X group in the $Cr(py)^{3+}$ series are as reactive as the corresponding $(NH_3)_5Cr(py)^{3+}$ complexes, yet the selectivity remains the same throughout the series of chromium complexes.

LFER Analysis. The Hammett equation has proved to be useful in similar circumstances.[1,11,12] Figure 2 shows attempted plots for $Cr(py)^{3+}$ and pyH^+ according to

$$\log k_X = \sigma\rho + \log k_0 \quad (13)$$

A least-squares fit of the data for $Cr(py)^{3+}$ resulted in a good correlation with a reaction constant $\rho = 7.2 \pm 0.4$. The values for pyH^+ gave a poorer correlation, but one that is at least acceptable. With the new values (X = 3-Cl and 4-Cl) included along with those previously reported,[12] $\rho = 6.6 \pm 1.9$. The latter parameter is valuable nonetheless, since it defines the standard for electron transfer directly to the pyridine ring. Possible reasons for a Hammett correlation that is less satisfactory than usually found are as follows: (a) Several of the reactions were complicated by spectral changes attributed to reaction intermediates. Although we have no reason to question seriously the validity of any of the values given, certain of them may have uncertainties larger than usually found in similar kinetic data. (b) The very essence of the Hammett method is that only electronic (inductive) interactions are to be measured; geometric influences, attractive or repulsive, are deliberately excluded. This reaction, involving electron transfer directly to the π^* orbitals of pyH^+, may experience effects of both sorts.

Reaction Mechanism. Taken alone, the data support the supposition that $Cr(py)^{3+}$ acts as an electron acceptor toward $^{\bullet}C(CH_3)_2OH$. Only when the trends are compared in detail with other cases[1,11,12,27-30] is it possible to address the question raised

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Table IV. Reaction Constants from Hammett LFER Correlations of Electron-Transfer Reactions of Pyridinium Ions and Metal–Pyridine Complexes

oxidizing agent	reducing agent	ρ	ref
Group A: Electron Transfer to Metal Known or Inferred			
$(NH_3)_5Co(NC_5H_4X)^{3+}$	$^{\bullet}C(CH_3)_2OH$	1.1	1
$(H_2O)_5Cr(NC_5H_4X)^{3+}$	$Ru(bpy)_3{}^+$	1.1	11
$(NH_3)_5Co(NC_5H_4X)^{3+}$	$Ru(NH_3)_6{}^{2+}$	1.3	1
$(NH_3)_5Co(NC_5H_4X)^{3+}$	$V(H_2O)_6{}^{2+}$	1.5	1
$(NH_3)_5Ru(NC_5H_4X)^{3+}$	$V(H_2O)_6{}^{2+}$	1.8	29
$(NH_3)_5Co(NC_5H_4X)^{3+}$	$Cr(H_2O)_6{}^{2+}$	1.9	30
Group B: Electron Transfer to Pyridine Known or Inferred			
$(H_2O)_5Cr(NC_5H_4X)^{3+}$	$^{\bullet}C(CH_3)_2OH$	7.2	*a*
$X\text{-}C_5H_4NH^+$	$^{\bullet}C(CH_3)_2OH$	8.5 (6.6 ± 1.9)	12, *a*
$X\text{-}C_5H_4NCH_3{}^+$	$^{\bullet}C(CH_3)_2OH$	9.0	12
$X\text{-}C_5H_4NCH_3{}^+$	$^*[Ru(bpy)_2(CN)_2]$	10.2	27
$X\text{-}2,6\text{-}Me_2C_5H_2NCH_3{}^+$	$^*[Ir(COD)(\mu\text{-}pz)_2]^b$	10.3	28

[a] This work. [b] COD = 1,5-cyclooctadiene; pz = pyrazolyl.

earlier as to the site of electron attack. The new results along with values from several sources are summarized in Table IV. As noted elsewhere,[1,11] all the data fall quite cleanly into one of two categories, those with "low" values of ρ (1.1–1.9) and those with "high" values (6.6–10.3). Each category contains some members where there is little doubt about the mechanism; all of those following a known mechanism fall in the expected group. On that basis we infer that reduction of $Cr(py)^{3+}$ occurs by electron transfer to the pyridyl ring.

The same conclusion might have been reached from different logic. Other Cr(III) complexes, lacking a pyridine ligand, react with this radical very slowly; e.g. for $Cr(H_2O)_6{}^{3+}$, $k = 5.6 \times 10^2$ $M^{-1}\ s^{-1}$,[19] and for $(H_2O)_5CrCl^{2+}$, $k < 3 \times 10^4\ M^{-1}\ s^{-1}$.[12b] Clearly, then, the *donor* ligand pyridine enhances the electron-transfer rate very substantially. This suggests that its effect is a consequence of its direct chemistry and is not an incidental feature.

The next step in the reaction sequence is suggested to be intramolecular electron transfer (as reported[31,32] on the basis of a direct measurement for a Co(III)–pyridyl radical complex) yielding the observed products.

$$Cr(py)^{3+} + {}^{\bullet}C(CH_3)_2OH \rightarrow (CH_3)_2CO + H^+ + [Cr^{III}py^{\bullet-}]^{2+} \tag{14}$$

$$[Cr^{III}py^{\bullet-}]^{2+} \rightarrow [Cr^{II}py]^{2+} \xrightarrow{H^+} Cr^{2+} + pyH^+ \tag{15}$$

An alternative possibility is that the immediate metal-bound radical product would, like the free $Hpy^{\bullet}$ radical, react by bimolecular disproportionation. We are inclined to discount that, however, in light of the products observed.

The LFER analysis of the reduction of the chromium and cobalt series by $^{\bullet}C(CH_3)_2OH$ poses a challenging question:[33] Will the relative reactivity of the two series become identical ($\rho = 10$) beyond the intersection point at $\sigma \sim 0.6$, i.e., when the reducibility of the ligand apparently exceeds that of the cobalt center? The answer may be difficult to obtain experimentally, since the rate constants in this region are high ($>10^8\ M^{-1}\ s^{-1}$) and the limitation imposed by the diffusion control may reduce the effect.

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Registry No. $(H_2O)_5Cr(NC_5H_5)^{3+}$, 34714-27-7; $(H_2O)_5Cr(NC_5H_4\text{-}4\text{-}CN)^{3+}$, 102436-45-3; $(H_2O)_5Cr(NC_5H_4\text{-}3\text{-}CN)^{3+}$, 42422-49-1; $(H_2O)_5Cr(NC_5H_4\text{-}4\text{-}Cl)^{3+}$, 102436-46-4; $(H_2O)_5Cr(NC_5H_4\text{-}3\text{-}Cl)^{3+}$, 42476-27-7; $(H_2O)_5Cr(NC_5H_4\text{-}4\text{-}t\text{-}Bu)^{3+}$, 102436-47-5; $HNC_5H_4\text{-}4\text{-}CN^+$, 37449-63-1; $HNC_5H_4\text{-}3\text{-}CN^+$, 53760-43-3; $^{\bullet}C(CH_3)_2OH$, 5131-95-3.

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Kinetic Studies on the Perchlorate Oxidation of Aqua Mo^{3+} and $Mo^{III}{}_2$

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The pale yellow hexaaqua Mo^{3+} ion and green aqua $Mo^{III}{}_2$ dimer $[(H_2O)_4Mo(OH)_2Mo(H_2O)_4]^{4+}$ are both oxidized by ClO_4^- in acidic solutions $[H^+] = 0.2\text{–}0.7$ M, $I = 1.0$ M, to the yellow Mo(V) aqua dimer, $[Mo_2O_4(H_2O)_6]^{2+}$. In each case three reaction stages are observed here referred to as involving induction, propagation, and termination. The behavior is quite different from that observed in all previous studies of ClO_4^- oxidations.

All reactions of perchlorate that it has been possible to study in any detail involve metal ions.[1] Each of the labile hexaaqua ions V^{2+} (−0.25 V), V^{3+} (0.36 V), and Ti^{3+} (~0.1 V) reduces ClO_4^- to Cl^- in an 8e⁻ process.[2,3] In the case of Ti^{3+} the rate law is rate = $(k_1 + k_2[H^+])[Ti^{3+}][ClO_4^-]$, and typical half-lives are up to 2 h at 40 °C.[3] With V^{2+}, rate constants are in the range $(5.3\text{–}7.6) \times 10^{-7}\ M^{-1}\ s^{-1}$ at 25 °C,[1,2,4] and with V^{3+}, the rate constant is $3.0 \times 10^{-6}\ M^{-1}\ s^{-1}$ at 50 °C.[2] Small contributions from $[H^+]$-dependent terms are also observed. Results for hexaaqua Ru^{2+} (0.23 V) with ClO_4^- are consistent with a substitution-controlled process ($3.2 \times 10^{-3}\ M^{-1}\ s^{-1}$), and ClO_3^- is the final product.[5] Although Cr^{2+} (−0.41 V) and Eu^{2+} (−0.38 V) are stronger reducing agents, there is little or no reaction with ClO_4^-,

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