Electron Transfer from Aliphatic Radicals to Ring-Substituted Pyridine *N*-Oxides and Their Cobalt−Ammine Complexes in Aqueous Solution[†]

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The reduction of pyridine *N*-oxides by 1-hydroxy-1-methylethyl radicals, $^{\bullet}CMe_2OH$, is acid-dependent, in accord with the greater reducibility of protonated pyridine *N*-oxides. The respective rate constants for the unprotonated (k_{R0}) and protonated (k_{R1}) pyridine *N*-oxides have the following values ($L\ mol^{-1}\ s^{-1}$): 8.1×10^7 and 2.8×10^9 (X = 4-CN), 7.5×10^6 and 3.7×10^8 (4-Cl), 7.8×10^6 and 8.4×10^7 (H), and 1.7×10^6 and 4.1×10^7 (4-Me). The reduction of the Co(III) complexes $(NH_3)_5Co(X\text{-}pyO)^{3+}$ by $^{\bullet}CMe_2OH$ is rapid ($k = 10^7$−$10^8\ L\ mol^{-1}\ s^{-1}$) and acid-independent. On the basis of linear free energy relationships it is concluded that the reduction of the Co(III) complexes takes place by a chemical mechanism, whereby $^{\bullet}CMe_2OH$ reduces the coordinated X-pyO followed by an intramolecular electron transfer to the cobalt center.

Introduction

Reductions of aromatic nitrogen heterocycles, particularly if they take place by an electron-transfer mechanism, pose an intriguing question as to the nature of the orbital interactions in the transition state. The substances we have in mind are, for example, pyridines, imidazoles, and (in this work) pyridine *N*-oxides (hereafter X-pyO, where X is a ring substituent). In each case we need to consider protonated forms as well as the free bases, since the reactions were investigated in acidic solutions over a range of pH. Kinetic studies have proved helpful in clarifying the operative mechanisms in certain of these instances, particularly with the inclusion of substituents that can probe the electron demand of these reagents toward a single electron donor.

Single-electron reduction of aromatic compounds yields transient free radicals. Such an electron-transfer event requires a powerful electron donor, which is one reason certain reducing aliphatic radicals have proved advantageous. In this research we have again utilized the 1-hydroxy-1-methylethyl radical as the electron donor. This choice offers the advantage of providing sufficient driving force for heterocycle reduction, since $E° \approx -1.2$ V for the half-reaction $Me_2CO + H^+ + e^- = {}^{\bullet}CMe_2OH$.[1] In addition, a donor of this constitution presumably will not interact or associate with the heterocyclic compound, as a transition-metal electron donor might. This feature allows a reliable comparison within and among the different families of heterocycles.

Of the donor radicals that one might choose for this task, one advantage of $^{\bullet}CMe_2OH$ is that it has been used in earlier work for related studies of pyridine[2,3] and imidazole[4,5] derivatives; its continued use for this series as well will enable comparisons between the new results and those already obtained without the need to compensate for another variation. Another reason for the selection of $^{\bullet}CMe_2OH$ has to do with a particular kinetic technique that allows the quantitative determination of rate constants over a range much wider than those accessible by techniques of flash photolysis and pulse radiolysis. The technique we have employed is the method of "stored free radicals",[3,6−8] which employs the organometallic cation $(H_2O)_5Cr{-}CMe_2OH^{2+}$, a species that reversibly releases the free radical. A steady state is set up, and the kinetics of the competitive reaction with the substrate of interest, here the pyridine *N*-oxide or its derivative, can be determined from the overall kinetics.

In these studies we report kinetic data for reduction of the free base and protonated forms of several pyridine *N*-oxides and for a series of cobalt(III) complexes having the general form $(NH_3)_5Co{-}ONC_5H_4X^{3+}$, hereafter $(NH_3)_5Co(X\text{-}pyO)^{3+}$. The cobalt complexes pose an additional question: does electron attack occur at the heterocyclic ring, as it obviously does in the absence of the metal center, or at the cobalt? Irrespective of the mechanism, Co_{aq}^{2+} would be the final product.

Linear free-energy relationships have proved useful in earlier work. The application of such treatments as the Hammett relationship to reactions of pyridine *N*-oxides may be less straightforward, however; for example, resonance effects enter here in ways that did not encumber the same treatment for pyridines and imidazoles. Parameters other than the Hammett σ constant can be used instead. The pK_a's of the protonated cations might serve, as might the standard reduction potential of the one-electron couple X-pyO/X-pyO$^{\bullet -}$.[9,10] In the absence of reliable potentials in aqueous solution, however, photoelectron spectroscopy was used to determine an alternative parameter.

[†] Dedicated to Radovan Marcec, our recently deceased colleague and friend.

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Table 1. UV−Visible Spectral Data for $[(NH_3)_5Co(ONC_5H_4X)]^{3+}$ Complexes

X	λ_1/nm	ϵ/L mol^{-1} cm^{-1}	λ_2/nm	$\epsilon/10^4$ L mol^{-1} cm^{-1}
4-CH_3O	520	118	297	1.29
4-CH_3	520	104	281	1.26
	522[a]	113[a]		
3-CH_3	518	99	280,[b] 255	1.1, 1.65
H	523	105	272	1.33
	521[a]	101[a]		

[a] Reference 14. [b] Shoulder.

Experimental Section

Materials. Commercially available pyridine *N*-oxides (unsubstituted, 4-CN, 4-CH_3, and 3-CH_3, Fluka; 4-CH_3O, Aldrich) were twice recrystallized from ethanol before use. 4-Chloropyridine *N*-oxide was synthesized from 4-nitropyridine *N*-oxide (Fluka) and acetyl chloride by a literature procedure.[11]

$[(NH_3)_5Co(X\text{-pyO})](ClO_4)_3$ salts were prepared from $[(NH_3)_5Co(H_2O)](ClO_4)_3$ and an excess of the corresponding X-pyO in DMF, according to the literature procedure for the pyridine complexes.[12] After decomposition in $HClO_4$, the complexes were analyzed for their cobalt[13] and X-pyO content by UV spectrophotometry. The spectroscopic characteristics of the cobalt complexes are given in Table 1. After these complexes were first prepared, another group reported the preparation of the pyO and 4-Me-pyO derivatives.[14]

Warning! Metal perchlorates are potentially explosive and should be handled with care.

Perchloric acid and hydrogen peroxide, both analytical grade Merck, were used without further purification. Lithium perchlorate was made from lithium carbonate (p.A. Merck) and perchloric acid and recrystallized three times from water. Isopropyl alcohol was redistilled weekly and kept in the dark. Hexaaquachromium(II) solutions were prepared by zinc-amalgam reduction of $[Cr(H_2O)_6](ClO_4)_3$ in aqueous $HClO_4$. The water was doubly distilled and purified in a Milli-Q purification system. Kinetic solutions were handled by glass syringes and platinum needles under an argon atmosphere. Commercial argon was passed over a copper catalyst and scrubbed through a Cr^{2+} solution.

Photoelectron Spectroscopy. Ionization potentials were determined in the gas phase by use of a Vacuum Generators UVG3 instrument, which was calibrated with small amounts of Ar and Xe.

The reduction potential for C_5H_5NO in aqueous solution was determined by differential pulse polarography (Polarographic Analyzer Model 174 A) on a hanging-mercury-drop electrode. At pH 2.5, $E = -1.03$ V vs Ag/AgCl (-0.81 V vs NHE) was obtained.

Kinetics. The source of the $^\bullet CMe_2OH$ radical was the organometallic cation $(H_2O)_5CrCMe_2OH^{2+}$, which was prepared by the modified Fenton reaction, as given in Scheme 1. This complex decomposes to nonradical products in a heterolytic process, referred to as acidolysis (eq 1), and to the desired free radical by reversible homolysis (S_H1), shown in eq 2. The model in eqs 1 and 2 was first reported in 1982 and verified by several subsequent tests.[15]

Scheme 1

$$Cr(H_2O)_6{}^{2+} + H_2O_2 \rightarrow (H_2O)_5Cr{-}OH^{2+} + HO^\bullet + H_2O$$

$$HO^\bullet + H{-}CMe_2OH \rightarrow H_2O + {}^\bullet CMe_2OH$$

$$Cr(H_2O)_6{}^{2+} + {}^\bullet CMe_2OH \rightarrow (H_2O)_5Cr{-}CMe_2OH^{2+} + H_2O$$

$$Cr{-}CMe_2OH^{2+} + H_3O^+ \rightarrow Cr_{aq}{}^{3+} + Me_2CHOH \qquad (1)$$

$$v_A = k_A[Cr{-}CMe_2OH^{2+}];\ k_A = k + k'[H_3O^+]$$

$$Cr{-}CMe_2OH^{2+} \rightleftarrows Cr_{aq}{}^{2+} + {}^\bullet CMe_2OH \qquad (2)$$

$$v_H = k_H[Cr{-}CMe_2OH^{2+}] - k_{Cr}[Cr_{aq}{}^{2+}][{}^\bullet CMe_2OH]$$

In the absence of oxygen and other reagents, the homolysis step is rapidly equilibrated ($k_H = 0.127$ s^{-1}; $k_{Cr} = 5.1 \times 10^7$ L mol^{-1} s^{-1} at 25 °C), and the irreversible acidolysis leads to the slow decomposition of the complex (k_A/s$^{-1} = 3.31 \times 10^{-3} + (4.91 \times 10^{-3})[H_3O^+]$ at 25 °C). In the presence of a substrate that reacts with the aliphatic free radical, however, the homolysis will be drawn toward completion. When the substrate is X-pyO, the reaction will occur as written in eq 3. The rate constant k_R is acid-dependent, as will be shown later.

$$^\bullet CMe_2OH + X\text{-pyO} \rightarrow Me_2C{=}O + X\text{-pyO}^{\bullet -} + H^+ \qquad (3)$$

$$v = k_R[Me_2C^\bullet OH][X\text{-pyO}]$$

The extent of the partitioning of the aliphatic radical between reactions 2 and 3 in a given experiment can be controlled by the adjustment of the (relative) concentrations of X-pyO and added $Cr_{aq}{}^{2+}$. With these two concentrations in considerable excess over that of the organochromium cation, the rate law for the overall loss of $CrCMe_2OH^{2+}$, after the steady-state approximation is made for $[{}^\bullet CMe_2OH]$, becomes

$$-\frac{d[CrCMe_2OH^{2+}]}{dt} = v = \left\{k_A + \frac{k_H k_R[X\text{-pyO}]}{k_R[X\text{-pyO}] + k_{Cr}[Cr_{aq}{}^{2+}]}\right\}[CrCMe_2OH^{2+}] \qquad (4)$$

The term in braces is a pseudo-first-order rate constant that we represent by $k_{obs.}$ In effect, the acidolysis pathway provides a minor correction, and the difference, $k_{obs} - k_A$, is the quantity to be correlated with the concentration variables. Rearrangement of the expression for k_{obs} provides a form in which the data can be linearized. As the resulting expression in eq 5 indicates, a plot of the inverse of the corrected rate constant is expected to be a linear function of the concentration ratio.

$$\frac{1}{k_{obsd} - k_A} = \frac{1}{k_H} + \frac{k_{Cr}}{k_R k_H}\frac{[Cr_{aq}{}^{2+}]}{[X\text{-pyO}]} \qquad (5)$$

The potentially interfering reactions between $Cr(H_2O)_6{}^{2+}$ and pyridine *N*-oxides[16] and some $(NH_3)_5Co(X\text{-pyO})^{3+}$ species[14] are slow and did not interfere with our kinetic study.

Results

All of the kinetic runs were performed with the concentrations of $Cr(H_2O)_6{}^{2+}$ and X-pyO or $(NH_3)_5Co(X\text{-pyO})^{3+}$ high enough compared to the concentration of $(H_2O)_5CrCMe_2OH^{2+}$ to ensure pseudo-first-order kinetics with respect to this species, the disappearance of which was followed at 311 nm by a Cary 219 spectrophotometer. The ratios of the two reagents competing for $^\bullet CMe_2OH$ were systematically varied.

The rate constants obtained, k_{obs}, were analyzed graphically according to eq 5. The rates of all of the pyridine *N*-oxide reactions were found to be acid-dependent, as illustrated in Figure 1.

The literature values of pK_a for X−pyOH$^+$ are[17]

4-CN	4-Cl	H	3-CH_3	4-CH_3	4-CH_3O
−1.17	0.36	0.79	1.08	1.29	2.05

The least basic compound, 4-CN-pyO, is protonated only to a maximum of 8% over the pH range used, and the measured rate constant is a linear function of $[H^+]$. The extent of

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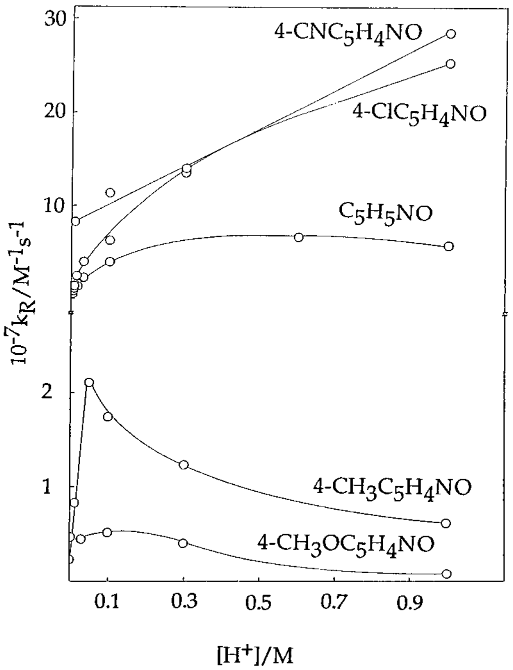

Figure 1. Dependence of the rate constants on [H^+] for the reactions of pyridine *N*-oxides with $^{\bullet}CMe_2OH$ at 25.0 °C. Conditions: [$(H_2O)_5CrCMe_2OH^{2+}$] = (2−5) × 10^{-5} M, [$Cr(H_2O)_6^{2+}$] = (2−29) × 10^{-4} M, [X-pyO] = (1.5 −20) × 10^{-4} M, and [$Cr(H_2O)_6^{2+}$]/[X-pyO] = 0.2−5.4.

Table 2. Second-Order Rate Constants for the Reduction of Substituted X-pyO, X-pyOH$^+$, and X-pyH$^+$ with 1-Hydroxy-1-methylethyl Radicals at 25 °C and 1.0 M Ionic Strength

X	X-pyO k_{R0}/L mol^{-1} s^{-1}	X-pyOH$^+$ k_{R1}/L mol^{-1} s^{-1}	X-pyH$^+$ k/L mol^{-1} s^{-1}
4-CN	8.1×10^7	2.8×10^9	($>6 \times 10^9$)[a]
4-Cl	7.5×10^6	3.7×10^8	2.6×10^6
H	7.8×10^6	8.4×10^7	9.6×10^5
4-CH$_3$	1.7×10^6	4.1×10^7	7.3×10^4

[a] Extrapolated to the diffusion-controlled limit from the Hammett relationship in ref 2.

protonation of 4-Cl-pyO reaches ~70%, and that of the unsubstituted pyO is ~85%. The acid dependence of these compounds levels off at high acidities, as the protonation nears completion. We assume that the terms which are independent of [H^+] and proportional to [H^+] are due to the respective reactions of the unprotonated and oxygen-protonated species, as shown in eq 6. After allowance is made for the proportioning of the reactant between acidic and basic forms, the linearized expression in eq 7 is obtained.

$$v = k_R[\text{X-pyO}]_T[^{\bullet}CMe_2OH] = \{k_{R0}[\text{X-pyO}] + k_{R1}[\text{X-pyOH}^+]\}[^{\bullet}CMe_2OH] \quad (6)$$

$$k_R\left(\frac{[H^+] + K_a}{K_a}\right) = k_{R0} + \left(\frac{k_{R1}}{K_a}\right)[H^+] \quad (7)$$

The most basic derivatives, 4-CH$_3$ and 4-CH$_3$O, show a real or apparent third term in their acidity dependence. We return to this unanticipated finding later, but for now the rate constants for the 4-CH$_3$ derivative are given only at low [H^+], where the two-parameter treatment remains valid. Table 2 lists the values of k_{R0} and k_{R1}. The rate constants for the corresponding pyridinium ions[2] are also given.

In several experiments the radical precursor $(H_2O)_5CrCMe_2OH^{2+}$ was replaced by the non-homolyzing $(H_2O)_5CrCH_2OH^{2+}$. As expected, no reduction of X-pyO took place. Moreover, the rate of acidolysis (0.01−1.0 M $HClO_4$) and the UV−visible spectrum of $(H_2O)_5CrCH_2OH^{2+}$ were both unchanged in the presence of 2 mM 4-Me-pyO, showing that 4-Me-pyO does not coordinate to $(H_2O)_5CrCH_2OH^{2+}$. On the basis of this result it seems safe to assume that pyridine *N*-oxides used in this work do not coordinate to $(H_2O)_5CrCMe_2OH^{2+}$ either.

The reduction of $(NH_3)_5Co(\text{X-pyO})^{3+}$ by $^{\bullet}CMe_2OH$ was straightforward and showed no acid dependence in the range 0.01−1.0 M $HClO_4$. The results are summarized in Table 3. The total amount of liberated X-pyO was always <10% of $[(NH_3)_5Co(\text{X-pyO})^{3+}]_0$, and there was no interference from the reaction of free X-pyO/X-pyOH$^+$ and $^{\bullet}CMe_2OH$.

Discussion

The radical $^{\bullet}CMe_2OH$ readily reduces all the pyridine *N*-oxides examined in this work. We presume that in each case X-pyH$^+$ is the final product, formed in the reaction between X-pyO$^{\bullet-}$ and excess Cr_{aq}^{2+} (eq 8), although this has not been verified experimentally. Facile reduction of coordinated X-pyO$^{\bullet-}$ by Cr_{aq}^{2+} has been proposed earlier as a rapid step in the reduction of pyO by Cr_{aq}^{2+}.[16]

$$\text{X-pyO}^{\bullet-} + Cr_{aq}^{2+} + 3H^+ \rightarrow \text{X-pyH}^+ + Cr_{aq}^{3+} + H_2O \quad (8)$$

Consistent with the presence of the *N*-oxide function, the rate constants are several orders of magnitude larger than those for the reduction of pyridines and imidazoles.[2,4,5] The observed acid dependence is readily explained by the acid−base equilibria (K_a) of pyridine *N*-oxides. As expected, the inductive effect of the proton increases the reactivity of X-pyOH$^+$ relative to X-pyO.

In addition to the k_{R0} and k_{R1} terms, the two most basic pyridine *N*-oxides (4-Me and 4-MeO) show an apparent third term at high [H^+], such that the reaction rate first increases and then decreases with acidity. No such term was observed for 4-CN-pyO, the unsubstituted pyO, or any of the X-pyO complexes of cobalt(III). We considered a possibility that the coordination of X-pyO to the radical precursor ($(H_2O)_5CrCMe_2OH^{2+}$) is responsible for this behavior, but this is unlikely in view of the complete lack of interaction between 4-Me-pyO and $(H_2O)_5CrCH_2OH^{2+}$.

Similarly, the second protonation of pyridine *N*-oxides (to X-pyO(H)$_2^{2+}$) might slow down the reduction, but there is no experimental or literature evidence for such protonation. In what follows, the discussion of the 4-Me and 4-MeO data will be limited to the low acidity range, where the two-term rate law applies.

In our earlier work on the reduction of pyridines and their metal complexes by $^{\bullet}CMe_2OH$, we have relied heavily on the Hammett ρ values as a mechanistic indicator.[2,3] For the reduction of the chromium complexes $(H_2O)_5Cr(\text{X-py})^{3+}$, the value of ρ (7.2) is similar to that for free X-pyH$^+$ ions (6.6), suggesting a chemical mechanism for the reduction of $(H_2O)_5Cr(\text{X-py})^{3+}$. The reaction is initiated by the reduction of the pyridine ligand, followed by intramolecular electron transfer to the metal. The cobalt series $(NH_3)_5Co(\text{X-py})^{3+}$ showed much less sensitivity to the substituent on the pyridine ($\rho = 1.1$), consistent with the direct reduction of the Co(III) center.

In the present work, the reactions of pyridine *N*-oxides and their cobalt complexes were subjected to the same analysis (Figure 2). The ρ values for the reduction of X-pyNO, X-pyNOH$^+$, and $(NH_3)_5Co(\text{X-pyO})^{3+}$ are all ~2 (1.8, 2.2, and 2.2, respectively). The much smaller ρ value for pyridine *N*-oxides compared to pyridines is consistent with the involve-

Table 3. Kinetic Data for the Reduction of $(NH_3)_5Co(X\text{-}pyO)^{3+}$ by 1-Hydroxy-1-methylethyl Radicals[a]

X of $(NH_3)_5Co(X\text{-}pyO)^{3+}$	$[Cr(H_2O)_6^{2+}]/10^4$ M	$[(NH_3)_5Co(X\text{-}pyO)^{3+}]/10^4$ M	$[Cr^{2+}]/[Co(III)]$	$k_R/10^7$ L mol^{-1} s^{-1}
H	2.6−12.2	2.3−5.4	0.99−3.8	7.7
3-CH_3	3.8−11	3.4−4.6	0.90−3.4	7.6
4-CH_3	5.9−12	3.8−6.0	0.99−2.8	4.0
4-CH_3O	4.2−8.4	2.4−5.4	1.0−2.4	2.0

[a] Conditions: 25 °C, $[H^+] = 0.01-1.0$ M, ionic strength 1.0 M ($HClO_4 + LiClO_4$), X-pyO = X-C_5H_4NO.

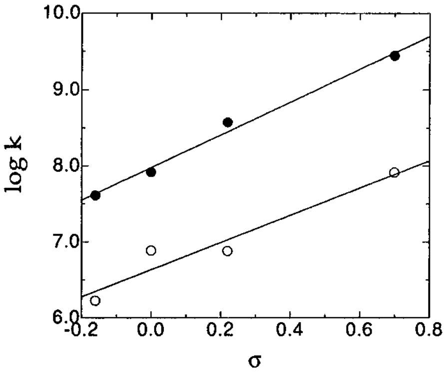

Figure 2. Plots of log k vs Hammett σ values for the reaction of $^{\bullet}CMe_2OH$ with X-pyO (filled circles) and X-pyOH$^+$ (open circles). Kinetic data are from Table 2 and σ values from ref 23.

Chart 1

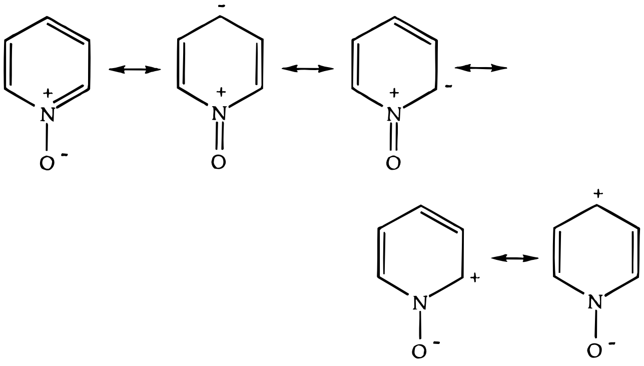

Table 4. First Ionization Potentials and Spectroscopic Data for Pyridine *N*-Oxides and Pyridinium Ions and Kinetic Data for the Reactions with 1-Hydroxy-1-methylethyl Radicals

X of X-pyO	log k_{R0}	log k_{R1}	E_i/eV[a]	λ_{max}/nm	$E_{\pi-\pi^*}$/eV	ΔE/eV[b]
4-CH_3	6.23	7.61	8.08	255	4.86	3.22
H	6.88	7.92	8.38	255	4.86	3.52
4-Cl	6.89	8.57	8.43	264	4.69	3.73
4-CN	7.91	9.44	9.02	282	4.39	4.63

X of X-$C_5H_4NH^+$ [c]	log k_{R1}	E_i/eV	λ_{max}/nm	$E_{\pi-\pi^*}$/eV	ΔE/eV
4-CH_3	4.86	9.41	263	4.71	4.70
H	5.98	9.66	255	4.85	4.81
4-Cl	6.41	10.01	257	4.81	5.19
3-Cl	7.87	9.83	271	4.57	5.25

[a] Ionization potentials are from refs 20−22. [b] See definition in eq 9. [c] data from refs 4 and 5.

ment of different resonance structures for *N*-oxides (Chart 1) and the known donor−acceptor interaction between the *N*-oxide oxygen and polar solvents.[18] Both of these effects modify the electron density at the reaction center.

The value of ρ for the protonated pyridine *N*-oxides has to be considered the lower limit, given that the rate constants for the most reactive derivatives approach the diffusion-controlled limit. The linearity of the Hammett plot through all the points indicates, however, that the true value of ρ is not much greater than 2.

The data strongly indicate that pyridine *N*-oxides and their cobalt complexes react by the same, chemical, mechanism: the attack by $^{\bullet}CMe_2OH$ at X-pyO, followed by an intramolecular electron transfer to the cobalt center of $(NH_3)_5Co(X\text{-}pyO)^{3+}$. An analogous mechanism operates in the reduction of some other Co(III) complexes. For example, an intermediate containing the one-electron-reduced *p*-nitrobenzoate ligand was observed directly in the study of the reduction of $(NH_3)_5Co(O_2CC_6H_4NO_2)^{2+}$ by $^{\bullet}CMe_2OH$.[19]

Further support for the chemical mechanism in the present work comes from the ρ value for the reduction of $(NH_3)_5Co(X\text{-}pyO)^{3+}$ being greater than that for $(NH_3)_5Co(X\text{-}py)^{3+}$, despite the smaller ρ value for the free X-pyO compared to the free pyridines. The following rate constants (L mol^{-1} s^{-1}) illustrate the different reactivity patterns in the pyridine and pyridine *N*-oxide systems:

$A_5Co-ONC_5H_5^{3+}$	ONC_5H_5	$^+HONC_5H_5$	$A_5Co-NC_5H_5^{3+}$	$^+HNC_5H_5$
7.7×10^7	7.8×10^6	8.4×10^7	1.2×10^7	9.6×10^5

The reduction of the free pyridinium ion is too slow for the cobalt to utilize an intramolecular path, and the cobalt center reacts by direct outer-sphere electron transfer from the radical. Pyridine *N*-oxide, which is reduced more easily than pyridinium ion, makes a chemical mechanism feasible, and the metal center is reduced in a secondary, intramolecular step. As noted by a reviewer, however, a direct attack at cobalt is always an available pathway.

Probably the best way to confirm the electron-transfer nature of a series of related reactions would be a correlation between the rate constants and the reduction potentials, $E_{1/2}$. Unfortunately, the $E_{1/2}$ values for 1e reduction of a series of X-pyO compounds are available only in DMF as solvent.[9] The rate constants for the reduction of both free and cobalt-complexed pyridine *N*-oxides by $^{\bullet}CMe_2OH$ (in water) are indeed linearly related to these $E_{1/2}$ values (in DMF). The meaning of the relationship is questionable, however, because the potentials for X-pyO must be very different (more positive) in H_2O than in DMF ($E_{1/2} = -1.4$ to -2.1 V for the compounds in this work); otherwise, the reduction by $^{\bullet}CMe_2OH$ ($E \approx -1.2$ V) would not be feasible. The expectation of the more positive $E_{1/2}$ in H_2O is also consistent with the stabilization of X-pyNO$^{\bullet-}$ by protonation and hydrogen bonding.[10] Indeed, the half-wave potential determined in this work for unsubstituted pyO, $E_{1/2} = -0.81$ V vs NHE at pH 2.5, is in full agreement with these expectations. The linearity of the plots of log k (in H_2O) against $E_{1/2}$ (in DMF) suggests that the relative orderings of the potentials for the various X-pyO's are comparable in DMF and H_2O.

Electrochemical data for pyridine *N*-oxides in water are available for the 2e processes,[10] but a correlation with these has not been sought. Instead, we examined the redox reactivity of pyridine *N*-oxides and their complexes as a function of a parameter related to electron affinity. We have utilized this

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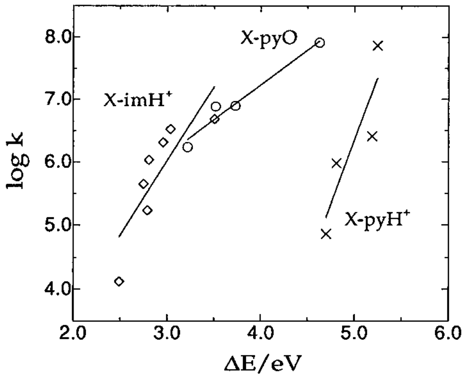

Figure 3. Plot of log *k* vs ΔE for the reaction of $^{\bullet}CMe_2OH$ with pyridine *N*-oxides (X-pyO, circles), pyridinium ions (X-pyH^+, crosses), and imidazolium ions (X-imH^+, diamonds). For the definition of ΔE see eq 9 and Table 4. Data for X-pyH^+ and imH^+ are from refs 4 and 5.

approach earlier in our work on imidazoles.[4,5] We were further encouraged in this attempt by a report[9] on linear correlation between the energy of the LUMO (from MO calculations) and the half-wave reduction potentials in DMF for pyridine *N*-oxides.

A measure of the electron affinity, denoted as ΔE in Table 4, was determined for pyridine *N*-oxides from the first ionization potentials E_i[20−22] for X-PyO and the energy of their lowest energy absorption maxima, $E_{\pi-\pi^*}$ (eq 9). The energy difference ΔE is taken as an estimate of the electron affinity of the π^* orbital.

$$\Delta E = E_i - E_{\pi-\pi^*} \qquad (9)$$

As shown in Figure 3, there is a good correlation between log *k* and ΔE for the reaction of X-PyO with $^{\bullet}CMe_2OH$, as well as for the corresponding reactions of pyridines and imidazoles published previously. This result provides additional support for the electron-transfer nature of all three series of reactions and of the reduction of $(NH_3)_5Co(X\text{-pyO})^{3+}$ by $^{\bullet}CMe_2OH$.

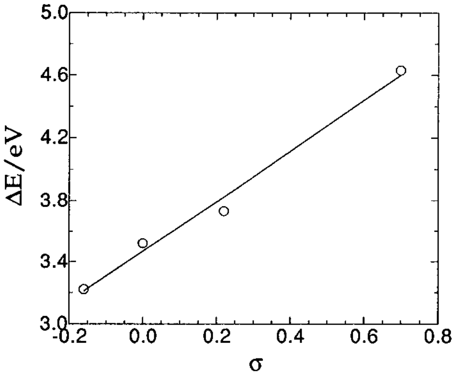

Figure 4. Plot of ΔE for X-pyO (eq 9) vs Hammett substituent constants σ.

The reduction of X-pyO is less sensitive to the change in ΔE than are the reductions of X-pyH^+ and imH^+, just as the Hammett ρ value is smaller for X-pyO than for X-pyH^+. This result increases our confidence in ΔE as a measure of the relative electron affinity within a series of related compounds. In fact, we find that there is a good linear correlation between ΔE and σ (Figure 4). This is especially encouraging in view of the reported correlation between the HMO-calculated energies of the LUMO and Hammett's σ values.[9]

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