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Preparation, Characterization, and Aquation Kinetics of Pyridine *N*-Oxide Complexes of Chromium(III)

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A series of $(H_2O)_5Cr(X\text{-pyO})^{3+}$ ions (pyO = pyridine *N*-oxide, X = H, 3-CH_3, 4-CH_3, 4-OCH_3, 4-NO_2) were prepared by the reduction of the corresponding pyridine *N*-oxide adducts of diperoxochromium(VI) species with acidic ferrous perchlorate. The $(H_2O)_5Cr(X\text{-pyO})^{3+}$ complexes undergo aquation to yield $Cr(H_2O)_6^{3+}$ and X-pyO according to the rate law $k_{obs} = k_o + k_{-1}[H^+]^{-1}$. The values of the rate constants extrapolated to 298 K at 1.0 M ionic strength are: $k_0 = 2.80 \times 10^{-6}\,s^{-1}$, $k_{-1} = 1.86 \times 10^{-8}\,M\,s^{-1}$ (X = 4-NO_2); 7.80×10^{-8}, 6.27×10^{-10} (H); 4.80×10^{-8}, 3.20×10^{-10} (3-CH_3); 3.05×10^{-8}, 1.60×10^{-10} (4-CH_3); and 2.37×10^{-9}, 4.76×10^{-11} (4-OCH_3). The reaction of the 4-OCH_3 complex exhibits two additional terms in the rate law, $k_1[H^+] + k_{-2}[H^+]^{-2}$. The binding of 4-$OCH_3$–pyO to chromium is suggested to take place through the methoxy group. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

Pyridine *N*-oxides (X-pyO) are important reagents in thermal[1,2] and photochemical[3–5] oxidations. Often, although not always,[6] such reactions involve oxygen-atom transfer[7–9] with pyridine *N*-oxide playing a role of either oxygen-atom donor[2,7–12] or a promoter of oxygen transfer from active donors to the substrate.[13–16] Metal catalysis is frequently involved[17] in such processes, which makes mechanistic studies of transition-metal complexes of pyridine *N*-oxides an important area of investigation.

A large number of complexes with an array of metal ions have been prepared and characterized structurally, spectroscopically, electrochemically, and chemically. There are, however, few reports available on the kinetics and mechanisms of the reactions of such complexes,[18–20] especially in aqueous solutions.[21,22] Several pentaamminecobalt(III) ions, $(NH_3)_5Co(X\text{-pyO})^{3+}$ have been prepared[21,22] and found to be reasonably stable at room temperature, provided there are no cyano substituents on the pyridine ring, in which case facile hydrolysis to a bound amide takes place.[21] The reduction of the parent $(H_2O)_5Co(pyO)^{3+}$ by chromium(II) is believed to take place by an inner-sphere mechanism whereby Cr_{aq}^{2+} attacks at the coordinated pyO oxygen,[21] although the expected product, $(H_2O)_5Cr(pyO)^{3+}$, was not observed, possibly because of its decomposition on ion-exchange resin. In the reduction of $(NH_3)_5Co(X\text{-pyO})^{3+}$ by 2-hydroxy-2-propyl radicals, $^{\cdot}C(CH_3)_2OH$, the initial site of attack was shown to be at the aromatic ring of the coordinated X-pyO.[23]

These studies have now been extended to a series of chromium complexes, $(H_2O)_5Cr(X\text{-pyO})^{3+}$ (X = H, 3-CH_3, 4-CH_3, 4-OCH_3, 4-NO_2). In this first report, we focus on the preparation and spectral and kinetic characterization of these complexes. Prior to this work, only the parent ion, $(H_2O)_5Cr(pyO)^{3+}$, was known.[24] It was generated by thermal equilibration of $Cr(H_2O)_6^{3+}$ with an excess of pyO in slightly acidic aqueous solutions at elevated temperatures, followed by ion exchange. In the present work, our previously published procedure for the preparation of pyridine chromium complexes[22] was applied to pyridine *N*-oxide analogues. This method represents a great advantage over the thermal equilibration method because it yields exclusively the mono-substituted products.

Results

The method used to prepare the complexes in Table 1 is based on the chemistry that we have developed earlier for the pyridine complexes.[22] By analogy to that work, the blue paste-like material generated from CrO_3, X-pyO and H_2O_2 is assigned the formula $CrO(O_2)_2(X\text{-pyO})$. Reduction with Fe_{aq}^{2+} produces the desired $(H_2O)_5Cr(X\text{-pyO})^{3+}$, Equation (1).

The chemical composition of the complexes was confirmed by chromium and ligand analysis after the complex had been allowed to aquate. In every case, the [Cr]/[X-pyO]

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Table 1. UV/Vis spectral data for $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ and X-pyO.

X	$(H_2O)_5Cr(X\text{-}pyO)^{3+}$ λ_{max} [nm] (ε, $M^{-1}\,cm^{-1}$)[a][b]			X-pyO λ_{max}, [nm] (ε, $M^{-1}\,cm^{-1}$)[c]	$XpyOH^+$
H	588 (25.7)	417 (30.5)	240 (1.15×10^4)	254 (1.15×10^4)	257 (2.9×10^3)
	586 (26.0)[d]	414 (30.8)[d]			217 (4.9×10^3)
3-CH_3	590 (25.9)	418 (31.7)	242 (1.08×10^4)	254 (1.17×10^4)	263 (3.5×10^3)
				209 (1.98×10^4)	220 (4.2×10^3)
4-CH_3	588 (29.8)	417 (40.9)	246 (1.35×10^4)	256 (1.40×10^4)	254 (2.7×10^3)
				206 (1.87×10^4)	226 (8.3×10^3)
4-OCH_3	582 (27.9)	417 (37.9)	262 (1.50×10^4)	261 (1.60×10^4)[b]	243 (1.20×10^4)[a][b]
4-NO_2	585 (33.6)	sh	266 (1.28×10^4)	313 (1.25×10^4)	280 (3.8×10^3)
				226 (8.0×10^3)	244 (8.2×10^3)

[a] In 1.0 M aqueous $HClO_4$. [b] This work. [c] Ref. [25]. [d] Ref. [24].

$$CrO(O_2)_2(X\text{-}pyO) + 7Fe_{aq}^{2+} + 10H^+ \rightarrow (H_2O)_5Cr(X\text{-}pyO)^{3+} + 7Fe_{aq}^{3+} \quad (1)$$

ratio was found to be 1.00 ± 0.02. As expected, the behavior of the complexes on the cation-exchange resin was consistent with a 3+ charge.

The UV/Visible spectroscopic data are summarized in Table 1. The spectrum of the unsubstituted material (X = H) agrees well with the literature data for a complex obtained by anation of $Cr(H_2O)_6^{3+}$ with pyO followed by ion-exchange to remove $Cr(H_2O)_6^{3+}$ and *cis*- and *trans*-$(H_2O)_4Cr(pyO)_2^{3+}$.[24]

The kinetics of aquation of $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ complexes were studied as a function of acidity and temperature at 1.0 M ionic strength. As illustrated in Figure 1 for $(H_2O)_5Cr(pyO)^{3+}$, the spectra exhibit clean isosbestic points as expected if the stoichiometry remains unchanged throughout the reaction, and no long-lived intermediates are involved.

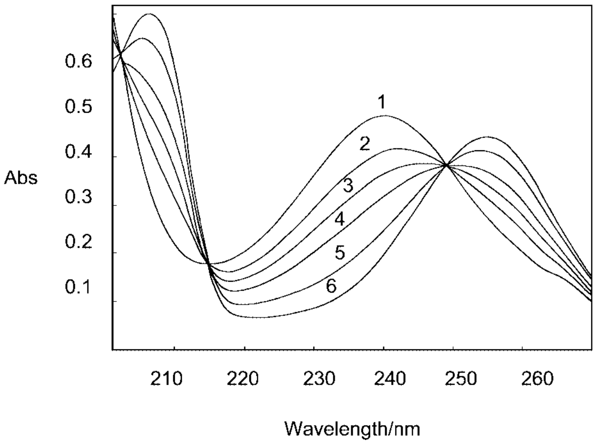

Figure 1. Spectral changes accompanying the aquation of $4.16\cdot10^{-5}$ M $(H_2O)_5Cr(pyO)^{3+}$ in 0.020 M $HClO_4$ at 1.0 M ionic strength and 90 °C. Spectrum **1** was obtained on a fresh sample at 25 °C before the onset of the reaction. Spectra **2** through **6** were measured at time 0 (arbitrary), 8, 18, 45.5, and 1250 minutes.

The standard treatment of the exponential kinetic traces yielded first-order rate constants k_{obs} which decreased with an increase in $[H^+]$ according to the expression in Equation (2) for all the complexes except for $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$, which exhibited a more complex behavior, see below.

$$k_{obs} = k_o + k_{-1}\,[H^+]^{-1};\ X = H,\ 3\text{-}CH_3,\ 4\text{-}CH_3,\ 4\text{-}NO_2 \quad (2)$$

The adherence to Equation (2) is shown for X = 3-CH_3 in Figure 2. The plot of k_{obs} against $1/[H^+]$ at several temperatures is linear yielding k_0 as an intercept and k_{-1} as a slope. Data for the remaining complexes (X = H, 4-CH_3, and 4-NO_2) are presented in the supporting information (Figures S1–S3; for supporting information see also the footnote on the first page of this article). The kinetic data are summarized in Table 2.

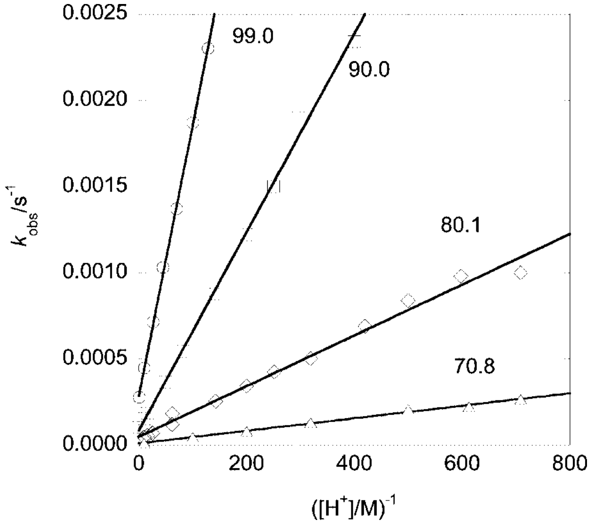

Figure 2. Plot of k_{obs} vs. $1/[H^+]$ for the aquation of $(H_2O)_5Cr(3\text{-}CH_3\text{–}pyO)^{3+}$ at 99.0 °C (circles), 90.0° (squares), 80.1° (diamonds), and 70.8° (triangles).

The activation parameters, also shown in Table 2, were obtained by fitting simultaneously all the individual acid-dependent rate constants k_{obs} for a given complex to the Eyring expression, Equation (3), where k_B and h are the Boltzman and Planck constants, respectively, T is the absolute temperature, and i = 0 and –1. The fit of the data to Equation (3) for $(H_2O)_5Cr(3\text{-}CH_3\text{–}pyO)^{3+}$ is shown in Figure 3, and for the rest of the complexes in Figures S4–S7 in the supporting information.

The plots of k_{obs} vs. $1/[H^+]$ for the 4-methoxy complex, Figure 4, exhibited deviations from Equation (2) at both the

Table 2. Summary of kinetic data for the aquation of $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ complexes.[a]

X	T [°C]	k_0 [s^{-1}][b]	k_{-1} [M s^{-1}][c]
4-NO_2[d]	70.2	$4.47(\pm0.27)\times10^{-4}$	$2.58(\pm0.14)\times10^{-5}$
	65	$2.92(\pm0.05)\times10^{-4}$	$1.15(\pm0.01)\times10^{-5}$
	60.2	$1.79(\pm0.13)\times10^{-4}$	$5.20(\pm0.09)\times10^{-6}$
	50.2	$5.64(\pm0.15)\times10^{-5}$	$1.31(\pm0.01)\times10^{-6}$
	40.1	$1.68(\pm0.17)\times10^{-5}$	$2.76(\pm0.10)\times10^{-7}$
	25.0	2.80×10^{-6} [e]	1.86×10^{-8} [e]
		$\Delta H_0^‡ = 93.9\pm2.2$	$\Delta H_{-1}^‡ = 129\pm3$
		$\Delta S_0^‡ = -36\pm6$	$\Delta S_{-1}^‡ = 40\pm8$
H	99.0	$3.7(\pm1.8)\times10^{-4}$	$1.95(\pm0.22)\times10^{-5}$
	90.0	$6.6(\pm4.8)\times10^{-5}$	$8.98(\pm0.21)\times10^{-6}$
	80.0	$1.2(\pm4.1)\times10^{-5}$	$2.20(\pm0.07)\times10^{-6}$
	70.0	$1.05(\pm0.14)\times10^{-5}$	$5.50(\pm0.05)\times10^{-7}$
	25.0	7.80×10^{-8} [e]	6.27×10^{-10} [e]
		$\Delta H_0^‡ = 104\pm47$	$\Delta H_{-1}^‡ = 125\pm4$
		$\Delta S_0^‡ = -32\pm127$	$\Delta S_{-1}^‡ = -1.6\pm10$
4-CH_3	98.6	$1.80(\pm0.29)\times10^{-4}$	$1.26(\pm0.04)\times10^{-5}$
	90.0	$9.96(\pm0.81)\times10^{-5}$	$3.82(\pm0.04)\times10^{-6}$
	80.1	$2.70(\pm0.54)\times10^{-5}$	$1.17(\pm0.02)\times10^{-6}$
	70.0	$6.6(\pm2.8)\times10^{-6}$	$3.00(\pm0.07)\times10^{-7}$
	25.0	3.05×10^{-8} [e]	1.60×10^{-10} [e]
		$\Delta H_0^‡ = 109\pm24$	$\Delta H_{-1}^‡ = 139\pm3$
		$\Delta S_0^‡ = -23\pm64$	$\Delta S_{-1}^‡ = 34\pm8$
3-CH_3	99.0	$2.87(\pm0.13)\times10^{-4}$	$1.57(\pm0.02)\times10^{-5}$
	90.0	$8.6(\pm2.2)\times10^{-5}$	$5.75(\pm0.11)\times10^{-6}$
	80.1	$4.8(\pm1.7)\times10^{-5}$	$1.47(\pm0.05)\times10^{-6}$
	70.8	$1.09(\pm0.50)\times10^{-5}$	$3.63(\pm0.11)\times10^{-7}$
	25.0	4.80×10^{-8} [e]	3.20×10^{-10} [e]
		$\Delta H_0^‡ = 104\pm21$	$\Delta H_{-1}^‡ = 134\pm2$
		$\Delta S_0^‡ = -36\pm56$	$\Delta S_{-1}^‡ = 23\pm6$
4-OCH_3[f]	99.3	$1.52(\pm0.10)\times10^{-4}$	$6.20(\pm0.08)\times10^{-6}$
	90.4	$5.03(\pm0.39)\times10^{-5}$	$1.98(\pm0.04)\times10^{-6}$
	80.0	$2.10(\pm0.37)\times10^{-5}$	$3.08(\pm0.29)\times10^{-7}$
	70.2	$3.95(\pm0.63)\times10^{-6}$	$8.75(\pm0.61)\times10^{-8}$
	25.0	2.37×10^{-9} [f]	$4.76(\pm0.39)\times10^{-11}$ [f]
		$\Delta H_0^‡ = 135\pm11$	$\Delta H_{-1}^‡ = 142\pm2$
		$\Delta S_0^‡ = 43\pm29$	$\Delta S_{-1}^‡ = 34\pm7$

[a] Ionic strength: 1.0 M ($HClO_4 + NaClO_4$). Units: $\Delta H^‡$ in kJ mol^{-1}, $\Delta S^‡$ in J mol^{-1} K^{-1}. [b] Obtained as intercept of k_{obs} vs. 1/[H^+] plots, as in Figure 2. [c] Obtained as a slope of k_{obs} vs. 1/[H^+] plots, as in Figure 2. [d] Additional data in 1.0 M $HClO_4$: 1.36×10^{-3} s^{-1} (80 °C), 8.43×10^{-4} (75 °C), 9.10×10^{-5} (55 °C). [e] Calculated from the activation parameters. [f] At >5 mM [H^+], a term directly proportional to [H^+] also contributes, $\Delta H_1^‡ = 104\pm43$ kJ mol^{-1}, $\Delta S_1^‡ = -48\pm115$ J mol^{-1} K^{-1}.

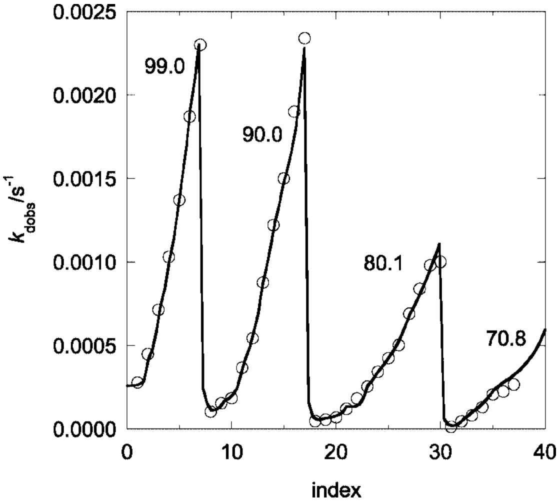

Figure 3. Fit of the data for the aquation of $(H_2O)_5Cr(3\text{-}CH_3\text{–}pyO)^{3+}$ to Equation 3 with use of the program Kaleidagraph 3.6. Index numbers on the x axis identify each unique point at a given acidity and temperature. Temperature (in °C) for each data set is indicated.

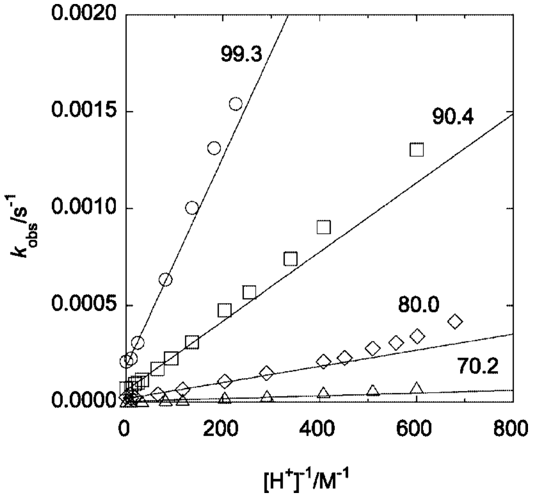

Figure 4. Plot of k_{obs} vs. 1/[H^+] for the aquation of $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$ at 1.0 M ionic strength.

$$k_{obs} = \frac{k_B T}{h}\sum_i [H^+]^i (e^{-\Delta H_i^‡/RT} e^{\Delta S_i^‡/R}) \tag{3}$$

$$k_{obs} = k_1[H^+] + k_o + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2};\ X = 4\text{-}OCH_3 \tag{4}$$

high and low ends of [H^+], and required two additional terms in the rate law, Equation (4), which is analogous to that reported for the azido complex, $(H_2O)_5CrN_3^{2+}$.[26]

The attempted fit of all the data to the multi-term Eyring expression of Equation (3) with i = 1, 0, –1, and –2 failed to converge, presumably because the contribution from the k_{-2} term was small and thus subject to large error under all of the conditions. The activation parameters in Table 2 were obtained by fitting only the data at >5 mM [H^+] to a 3-term variant of Equation (3), i.e., i = 1, 0, and –1. The rather large errors, especially for the less prominent terms, were to be expected for a complex fit and a large number of parameters.

To ascertain that the k_1 term is real and not a result of misinterpreted deviations from a simpler rate law, several experiments were conducted at higher acid concentrations at 4.0 M ionic strength where k_1 and k_0 terms should dominate. The results are shown in Figure 5, which clearly confirms the expectations. The rate constants at 99.0 °C are $k_0 = 2.20(\pm0.14)\times10^{-4}$ s^{-1} and $k_1 = 1.16(\pm0.07)\times10^{-4}$ M^{-1} s^{-1}. The corresponding values extracted from the more complex set of data at 1.0 M ionic strength are $k_0 = 1.52(\pm0.11)\times10^{-4}$ s^{-1} and $k_1 = 5.6(\pm1.9)\times10^{-5}$ M^{-1} s^{-1}.

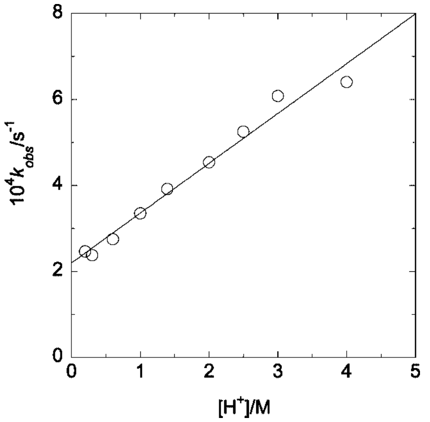

Figure 5. Plot of k_{obs} vs. $[H^+]$ for the aquation of $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$ at 4.0 M ionic strength and 99 °C.

Discussion

UV/Vis Spectra: The ligand-field transitions for all the pyridine *N*-oxide complexes studied (Table 1) are red-shifted relative to the corresponding pyridine complexes,[22] consistent with the greater ligand-field strength of the pyridines.

With the exception of the 4-OCH_3 derivative, the positions of the UV bands for $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ ions are considerably different from those of the free ligands. As an example, $(H_2O)_5Cr(4\text{-}CH_3\text{–}pyO)^{3+}$ in 1 M H^+ exhibits a maximum at 246 nm ($\varepsilon = 1.35\times10^4$ M^{-1} cm^{-1}). Under the same conditions, the free ligand has maxima at 254 nm ($\varepsilon = 2.7\times10^3$) and 226 nm ($\varepsilon = 8.3\times10^3$). In neutral solutions, these maxima shift to 256 nm ($\varepsilon = 1.40\times10^4$) and 206 nm ($1.9\times10^4$). Similar spectral differences between the free and Cr-bound pyridine *N*-oxides are observed for the rest of the materials in Table 1. Only the spectrum of $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$ ($\lambda_{max} = 262$ nm, $\varepsilon = 1.50\times10^4$ M^{-1} cm^{-1}) is almost identical to that of the free ligand in H_2O. This observation suggests that the binding of 4-OCH_3–pyO to chromium perhaps takes place at the methoxy oxygen, whereas the rest of the complexes utilize the pyridine oxide oxygen. We rationalize this assignment by noting that coordination via the methoxy group should affect the intraligand charge-transfer transitions to a lesser extent than coordination via the *N*-oxo group, or the protonation of the *N*-oxo group. Additional arguments in favor of the unique binding mode in $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$ will be presented shortly.

Kinetics of Aquation of $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ (X = H, 3-CH_3, 4-CH_3, 4-NO_2): The two-term rate law of Equation (2) is common to all the complexes with the exception of the 4-methoxy derivative which exhibits two additional terms, $k_1[H^+]$ and $k_{-2}[H^+]^{-2}$, Equation (4). The rate law of Equation (2) is typical for the aquation of pentaaquachromium(III) complexes, including those of the closely related $(H_2O)_5Cr(X\text{-}py)^{3+}$ ions. A reasonable mechanism features parallel reactions of the pentaaqua complex and its conjugate base, Equations (5), (6) and (7) leading to the rate law in Equation (8). In the limit $K_a << [H^+]$, Equation (8) reduces to the observed form, Equation (2), where $k_{-1} = k_{-1}'K_a$.

$$(H_2O)_5Cr(4\text{-}X\text{-}pyO)^{3+} \rightleftharpoons (H_2O)_4(OH)Cr(4\text{-}X\text{-}pyO)^{2+} + H^+ \quad K_a \tag{5}$$

$$(H_2O)_5Cr(4\text{-}X\text{-}pyO)^{3+} \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + 4\text{-}X\text{-}pyO \quad k_0 \tag{6}$$

$$(H_2O)_4(OH)Cr(4\text{-}X\text{-}pyO)^{2-} \xrightarrow{H_2O} (H_2O)_5CrOH^{2+} + 4\text{-}X\text{-}pyO \quad k_{-1}' \tag{7}$$

$$k_{obs} = \frac{k_0[H^+] + k_{-1}'K_a}{K_a + [H^+]} \tag{8}$$

The acidity constants for the pyridine oxide complexes have not been determined, but the excellent fit of the data to Equation (2) throughout the acid range studied places a limit $K_a << 10^{-3}$ M for all the complexes in the temperature range examined.

The activation enthalpies are large for both pathways for all the complexes. Activation entropies are moderately negative for the k_0 path, and moderately positive for the k_{-1} path. The only exception seems to be the parent pyO complex, for which $\Delta S_{-1}^{\ddagger}$ is close to zero (-1.6 ± 10 J mol^{-1} K^{-1}). These results are consistent with a strong associative component in the k_0 path, as is often the case with aqua Cr^{III} complexes, including the water substitution in $Cr(H_2O)_6^{3+}$.[27] The k_{-1} path is a composite, which makes the mechanistic assignment of the kinetic step more difficult to make. Still, given that the ΔS^0 component (associated with the K_a) will be positive, and the overall $\Delta S_{-1}^{\ddagger}$ is only on the order of 20–40 J mol^{-1} K^{-1}, one can all but rule out a strong dissociative contribution to k_{-1}. The data are consistent with an interchange mechanism in either dissociative or associative regime.

The Case of $(H_2O)_5Cr(4\text{-}OCH_3\text{-}pyO)^{3+}$: As already mentioned, the aquation of aqua and amine complexes of chromium(III) often follows the general rate law of Equation (2). The direct dependence on $[H^+]$, on the other hand, has been observed only for those complexes that have a ligand with an open basic site, i.e. anions such as F^-, N_3^-, SO_4^{2-}, CN^-, or CH_3COO^-.[28–32] This path is not expected to operate for $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ complexes; the basicity of X-pyO oxygen is greatly reduced upon coordination to Cr, and the probability of protonation is minimal. The complexes having X = H, 3-CH_3, 4-CH_3, and 4-NO_2 follow this prediction and do not feature a $k_1[H^+]$ term. The 4-OCH_3 derivative, on the other hand, has a pronounced $k_1[H^+]$ term which would be difficult to explain for a complex having a Cr–oxopyridine bond, Cr–Opy(4-OCH_3). If, however, the ligand is coordinated through the methoxy group, as in Cr–O(CH_3)pyO, then the protonation at the exposed pyO oxygen becomes more likely. We suggest that bonding through the methoxy group indeed takes place and is responsible for the unique behavior of the 4-OCH_3–py complex. The UV spectrum discussed earlier supports this assignment. Even though the basicity of the methoxy oxygen should be greatly diminished in the chromium complex as compared to the free base, the protonation can still take place at the high end of $[H^+]$ used in this work. The proposed isomer, $(H_2O)_5$Cr–O(CH_3)pyO^{3+}, should not be considered an unusual species in that related alcohol complexes of Cr^{III}, such as $(H_2O)_{6-n}Cr[O(H)CH_3]_n^{3+}$, are well known and quite stable.[33]

The positive $\Delta S_0^\ddagger$ value for $(H_2O)_5Cr(4\text{-}OCH_3\text{–}pyO)^{3+}$, $43 \pm 29\ J\,mol^{-1}\,K^{-1}$, seems outstanding, and may suggest a mechanistic deviation from the associative interchange assigned to the rest of the complexes in Table 2. The large error bars for all the entropy values in Table 2, however, make such a conclusion uncertain. We also note that an unexplained positive $\Delta S_0^\ddagger$ term was observed in the aquation of $(H_2O)_5Cr(3\text{-}CH_3\text{–}py)^{3+}$,[22] which does not appear outstanding in any other respect.

The k_{-2} path was observed only for $(H_2O)_5Cr(4\text{-}CH_3O\text{–}pyO)^{3+}$, implying a greater acidity of the coordinated waters for this complex. This is a surprising observation and contrary to what one might expect on the basis of the strong electron donation from the 4-methoxy group and the greater basicity of 4-CH_3O–pyO[34] compared to other pyridine oxides in this work. It is not clear whether the different binding mode to Cr^{III} would cause the observed shift in the pK_a.

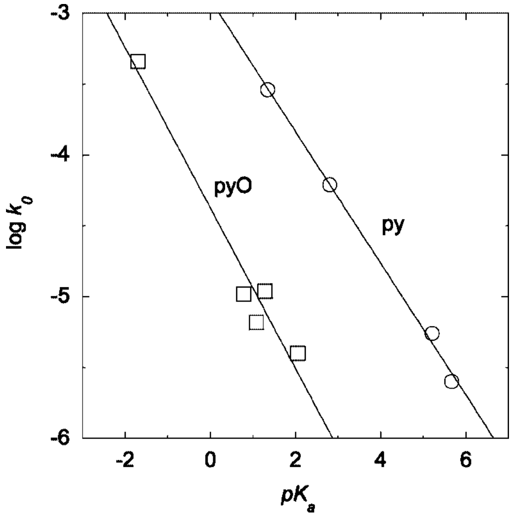

Figure 6. Plot of logk_0 vs. pK_a of the free ligands for the aquation of $Cr(H_2O)_5^{3+}$ complexes of pyridines (py, circles) and pyridine *N*-oxides (pyO, squares) at 70 °C. The substituents on pyO, in the order of increasing pK_a, are 4-NO_2, H, 3-CH_3, 4-CH_3, and 4-OCH_3. In the pyridine series, the order is 3-CN, 3-Cl, H, 3-CH_3. Data are from Table 2 and references [22], [23] and [34].

Comparison with Pyridine Complexes: Figure 6 shows a plot of the logarithms of the first-order rate constants k_0 against the pK_a of the protonated ligands for complexes of Cr^{III} with pyridines and pyridine *N*-oxides at 70 °C. The correlation was not sought for k_{-1}, which is a composite of rate and acid dissociation constants.

Both sets of rate constants in Figure 6 are linearly related to the ligand pK_a, a measure of σ electron donation. In both cases, the greater thermodynamic affinity for the proton results in a kinetically more inert chromium complex, i.e. the greater the pK_a the slower the aquation. When the two series are compared to each other, however, then the pK_a argument breaks down; the less basic pyridine *N*-oxides bind to the chromium more strongly, at least in the kinetic sense. One obvious source of the apparent anomalous inertness of pyridine *N*-oxide complexes is the greater ability of pyridine *N*-oxides to engage in π-bonding with the metal.

Experimental Section

Preparation of Complexes. $(H_2O)_5Cr(pyO)^{3+}$: To a stirred, ice-cold aqueous solution (2 mL) of 1 M pyridine oxide (PyO) and 1 M CrO_3 was added dropwise cold 30% H_2O_2 (2 mol-equiv.). The resulting blue paste was immediately treated with a solution containing 7.5 mol-equiv. of ferrous perchlorate and 11 mol-equiv. of $HClO_4$. The green product solution was loaded onto a column of Dowex 50W-X8 cation-exchange resin. Iron(III) ions were eluted with 0.1 M NaSCN in 1 M $HClO_4$. The column was rinsed with 1 M $HClO_4$ to remove the remaining NaSCN. Chromium(III) species were eluted with 3 M $HClO_4$ and collected in several fractions. The blue $Cr(H_2O)_6^{3+}$ was eluted first, followed by the green $(H_2O)_5Cr(pyO)^{3+}$. The middle fraction of this complex was used for all the kinetics and spectral measurements. The same procedure was used to prepare the ring-substituted complexes $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ (X = 3-CH_3, 4-CH_3, 4-CH_3O and 4-NO_2), except that in the case of $(H_2O)_5Cr(4\text{-}NO_2\text{–}pyO)^{3+}$, the solvent water in the initial step was replaced by a 1:1 H_2O/dioxane mixture to increase the solubility of the ligand.

Materials: Pyridine *N*-oxides (pyO, 3-CH_3–pyO, 4-CH_3–pyO, and 4-NO_2–pyO) were purchased from Fluka and recrystallized twice from ethanol. 4-CH_3O–pyO was prepared by refluxing 28 g 4-NO_2–pyO (Fluka) and 28 g K_2CO_3 in 200 mL of methanol for 8 hours.[35] The product was recrystallized twice from heptane. Solutions of iron(II) perchlorate were prepared by zinc amalgam reduction of the Fe^{III} salt. Sodium perchlorate was prepared from perchloric acid and sodium carbonate. The solid was recrystallized three times from doubly distilled water. Other chemicals were purchased at the highest purity available and used as received.

Analyses: The chromium content of $(H_2O)_5Cr(X\text{-}pyO)^{3+}$ was determined spectrophotometrically after oxidizing the chromium to chromate ($\varepsilon_{372} = 4.82 \cdot 10^3\ M^{-1}\,cm^{-1}$)[36] with alkaline hydrogen peroxide. The concentration of the appropriate pyridine *N*-oxides generated by hydrolysis of the complex in 0.10 M $HClO_4$ for ≥ 10 half-lives was determined spectrophotometrically.

Kinetic Measurements: The aquation of all the complexes was monitored spectrophotometrically at a wavelength, typically close to λ_{max} for the free ligand, where the difference in molar absorptivities for reactants and products was at a maximum. The initial concentration of all the complexes was in the range 3–30 μM. In most cases, the change in absorbance was monitored continuously inside a thermostatted cell compartment of a Cary 17 spectrophotometer. In some experiments, especially those at ≥ 90 °C, the samples were sealed in glass ampoules and immersed into thermostatted (±0.05 °C) oil. At the desired times, an ampoule was removed, and the reaction quenched in either ice-cold water or liquid nitrogen. The sample was brought to room temperature to record the absorbance. The rate constants and activation parameters were obtained by fitting the data to appropriate equations with the program Kaleidagraph 3.6.

Supporting Information (see also the footnote on the first page of this article): Figures S1–S7, kinetic data.

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