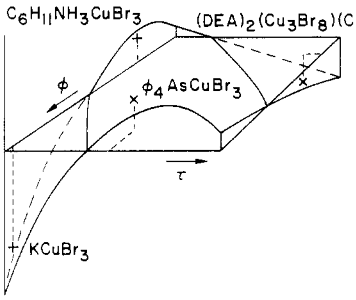

Figure 6. Schematic illustration of the $J(\phi,\tau)$ surface for symmetric bibridged copper(II) systems.

for the bromide salts in agreement with the results of this study.

The effect of changing the coordination geometry from square planar toward tetrahedral was also examined by Hay et al.[29] This distortion is characterized by the dihedral angle, τ, between the planes defined by the terminal CuX$_2$ fragment and the bridging CuX$_2$ fragment. For a ϕ value such that $J < 0$, it was found that, as ϕ increases from 0°, the interaction first becomes positive ($J > 0$), reaching a maximum, and then becomes negative again as ϕ approaches 90°. Experimentally, it is found that the planar dimer in KCuCl$_3$[22] is antiferromagnetic, while the twisted dimers in Ph$_4$AsCuCl$_3$[34] and Ph$_4$PCuCl$_3$[35] are ferromagnetic.

As indicated in the Introduction, structures are not known on many copper(II) bromide salts. Assuming isomorphism with the corresponding chlorides, we can begin to examine the magneto–structural correlations in the bromide series. For the planar dimers in KCuBr$_3$[36] and NH$_4$CuBr$_3$[16] ($\phi \sim 95°$; $\tau = 0°$), antiferromagnetic behavior is observed with $J/k \sim -100$ K. In (C$_6$H$_{11}$NH$_3$)CuBr$_3$ ($\phi \sim 86°$; $\tau = 0°$),[37] ferromagnetic behavior is found with $J/k \sim 60$ K. (It is noted that the copper geometry is square pyramidal and other distortions exist. However, $J > 0$ is also found in CuBr$_2$·Me$_2$SO,[38] where $\phi = 86°$.) Then in Ph$_4$AsCuBr$_3$[39] and Ph$_4$PCuBr$_3$[35] ($\phi \sim 93°$; $\tau \sim 48°$), ferromagnetic interactions are again found with $J/k \sim 30$ K. To this we add the results of this study where we have, for the trimer ($\phi \sim 94°$; $\tau = 0°$), $J/k = -100$ K and, for the chain ($\phi \sim 84°$; $\tau \sim 86°$), $J/k = -20$ K. These results can be interpreted qualitatively in terms of the $J(\phi,\tau)$ surface drawn schematically in Figure 6. For the lines with $\tau = 0°$ and with $\phi \sim 95°$, the qualitative features of the theoretical predictions of Hay et al.[29] are incorporated with the remainder of the curve deduced from eq 1. We see that a ferromagnetic ridge exists in the surface, with the antiferromagnetic trimer lying on one side of the ridge and the antiferromagnetic chain lying on the opposite side.

Finally, it is appropriate to comment on the difference between the approach we have taken in discussing magneto–structural relationships in systems with multiple structural parameters and those taken by several other authors. We are seeking to map out a hypersurface of the type, for example, $J(\phi,\tau)$. Contrariwise, it has been proposed, in hydroxy-bridged Cr(III) dimers[40] and in asymmetrical bridged copper(II) halide salts,[41] that J depends only on the ratio ϕ/R, where ϕ is the bridging angle and R is the Cr–O or the axial Cu–Cl distance. The latter can be valid in two situations if there is a strong correlation between the two parameters, ϕ and R: this may occur, for example, if (1) the bridging ligand–ligand repulsions determining the bridging geometry or (2) the paths of constant ϕ/R are essentially parallel to contours of constant J. It is clear, in any case, that a ratio of structure parameters such as ϕ/R only samples a portion of the total surface defining the exchange energy.

Acknowledgment. This work was supported by NSF Grant No. CHE-77-08610.

Registry No. (DEA)$_2$Cu$_4$Br$_{10}$·EtOH, 83632-64-8.

Supplementary Material Available: Listings of positional and thermal parameters and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Kinetics of the Reduction of Pyridinium Ions by 2-Hydroxy-2-propyl Radicals in Aqueous Solution

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Kinetic measurements were made for the reductions of the pyridinium ions derived from pyridine, 4-methylpyridine, 3-hydroxypyridine, nicotinamide, and isonicotinamide as well as 1-methylpyridinium and 1,4-dimethylpyridinium ions by 2-hydroxy-2-propyl radicals, which were generated by the homolytic cleavage of the chromium–carbon bond in (H$_2$O)$_5$CrC(CH$_3$)$_2$OH^{2+}. The rate constants (dm^3 mol^{-1} s^{-1}) at 25.0 °C and an ionic strength of 1.0 M (LiClO$_4$) are as follows: pyridinium ion, 9.6×10^5; 1-methylpyridinium ion, 3.7×10^5; 4-methylpyridinium ion, 7.3×10^4; 1,4-dimethylpyridinium ion, $\leq 1 \times 10^4$; 3-hydroxypyridinium ion, 1.4×10^8; 3-(aminocarbonyl)pyridinium ion, 7.9×10^8; 4-(aminocarbonyl)pyridinium ion, 1.2×10^9. The rate constants are reasonably well correlated by the Hammett ρ–σ equation with $\rho = +8.5$. The first two compounds show a second kinetic term corresponding to the rate law $k'[\mathrm{Cr}^{2+}][\mathrm{pyH}^+][\cdot\mathrm{C}(\mathrm{CH}_3)_2\mathrm{OH}][\mathrm{H}^+]^{-1}$, consistent with reduction of a Cr(II)–pyridine complex by the free radical.

Introduction

Homolytic cleavage of the chromium–carbon bond in (H$_2$O)$_5$CrC(CH$_3$)$_2$OH^{2+} is a ready source of 2-hydroxy-2-propyl radicals and, as recently demonstrated,[1] can be used for kinetic studies of the reactions of 2-hydroxy-2-propyl radicals in acidic solutions. Reductions of cobalt(III)–amine

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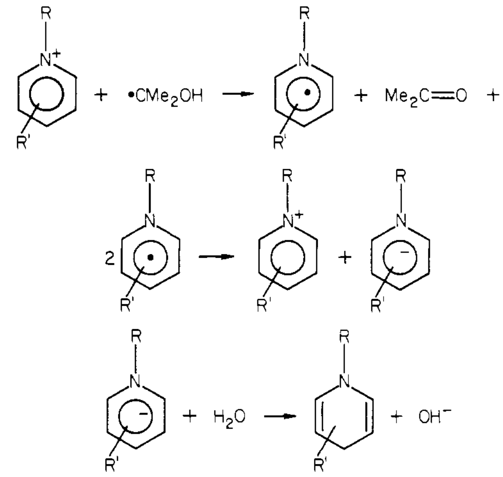
Table I. Summary of Kinetics of the Reduction of Pyridinium Ions by 2-Hydroxy-2-propyl Radicals[a]

pyridinium ion	concn ranges/M			k_2/M^{-1} s^{-1} [b]
	$[H^+]$	$10^3[Cr^{2+}]$	$10^3[pyH^+]$	
$4\text{-}CH_3C_5H_4NCH_3{}^+$	0.0104–0.0979	1.07–4.40	8.92–18.0	$\leq 1 \times 10^4$
$4\text{-}CH_3C_5H_4NH^+$	0.00741–0.103	4.40–11.1	24.2–104	7.3×10^4
$C_5H_5NCH_3{}^+$	0.015–0.103	2.74–9.40	6.77–17.2	3.7×10^5
$C_5H_5NH^+$	0.0120–0.259	4.40–19.4	5.00–54.0	9.6×10^5
$3\text{-}OHC_5H_4NH^+$	0.046–0.203	16.1	2.65–9.36	1.4×10^8
$3\text{-}(CONH_2)C_5H_4NH^+$	0.041–0.080	41.1–83.0	1.95–4.88	7.9×10^8 [c]
$4\text{-}(CONH_2)C_5H_4NH^+$	0.077–0.232	16.7–83.3	1.56–5.47	1.2×10^9 [d]

[a] At 25.0 °C and $\mu = 1.0$ M. [b] k_2 is calculated according to eq 3 by using literature values of k_A, k_1, and k_{-1}. [c] Pulse radiolysis values are 4.0×10^8 [5] and 2.1×10^8.[6] [d] The pulse radiolysis value is 3.1×10^9.[6]

Scheme I



complexes were described previously,[1] and in the present work we have investigated the reductions of pyridine derivatives in acidic aqueous solutions. Radical reactions of aromatic N-heterocyclic compounds are particularly interesting because of their possible participation in biochemical reactions of pyridine nucleotides and because of synthetic possibilities in homolytic substitutions of aromatic rings.[2-4]

Pulse-radiolytic studies of reductions of substituted pyridines by $\cdot CMe_2OH$ radicals have been reported.[5,6] Pyridine derivatives are reduced to form pyridinyl radicals, which disproportionate to pyridines and hydropyridines (Scheme I).[5] Electron transfer and radical addition to coordinated polypyridines have also been studied.[7,8]

However, pyridine itself and pyridines having simple substituent groups such as CH_3 have not been investigated. This paper describes the reductions of the pyridinium ions derived from pyridine, methylpyridines, hydroxypyridine, nicotinamide, and isonicotinamide. The last two systems provide a good test of our measurements using an organochromium complex as the radical source, since they have also been studied by pulse radiolysis.

Experimental Section

Materials. Pyridinium perchlorate,[9,10] 1-methylpyridinium iodide,[11] and 1,4-dimethylpyridinium iodide[12] were prepared by literature methods. 4-Methylpyridinium perchlorate, 3-hydroxypyridinium perchlorate, 3-(aminocarbonyl)pyridinium perchlorate, and 4-(aminocarbonyl)pyridinium perchlorate solutions were prepared by neutralizing the respective bases with perchloric acid.

The solutions of $CrCMe_2OH^{2+}$ were prepared from $Cr(H_2O)_6{}^{2+}$ and hydrogen peroxide in the presence of 0.35 M 2-propanol.[13,14]

Kinetic Procedure. All the reactions were carried out under a nitrogen atmosphere, at an ionic strength of 1.0 M ($LiClO_4$) and 25.0 °C. The reactions were initiated by injection of a pyridine solution into a solution containing $CrCMe_2OH^{2+}$ using anaerobic syringe techniques. Reactions were followed by using a Cary Model 219 spectrophotometer to monitor the decrease in absorbance at or near an absorption maximum of $CrCMe_2OH^{2+}$: 311 nm ($\epsilon = 2500$ dm^3 mol^{-1} cm^{-1}) or 407 nm ($\epsilon = 700$ dm^3 mol^{-1} cm^{-1}). Some reactions were followed at 320 or 340 nm to escape strong absorption due to pyridines. In the nicotinamide reaction, exceptional absorbance changes were observed. The absorbance at 340 nm increased initially and then slowly decreased. Details are described under Results.

The kinetics obeyed a first-order rate law, and the data were analyzed by standard methods. The observed pseudo-first-order rate constant, k_{obsd}, is related[1] to the rate constant for reaction 2 through eq 3, where pyH^+ is a general designation for all of the pyridinium ions and where k_A denotes the rate constant for acidolysis of $CrCMe_2OH^{2+}$ (eq 4; k_A (s^{-1}) $= 3.31 \times 10^{-3} + 4.91 \times 10^{-3}[H^+]$) and

$$CrCMe_2OH^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr^{2+} + \cdot CMe_2OH \tag{1}$$

$$\cdot CMe_2OH + pyH^+ \xrightarrow{k_2} Me_2C{=}O + H^+ + \text{pyridinyl radical} \tag{2}$$

$$k_{obsd} = k_A + \frac{k_1}{1 + k_{-1}[Cr^{2+}]/k_2[pyH^+]} \tag{3}$$

$$CrCMe_2OH^{2+} + H^+ = Cr^{3+} + Me_2CHOH \tag{4}$$

k_1 and k_{-1} are the rate constants of homolysis of $CrCMe_2OH^{2+}$ ($k_1 = 0.127$ s^{-1})[14] and recombination of Cr^{2+} and $\cdot CMe_2OH$ radicals ($k_{-1} = 5.1 \times 10^7$ M^{-1} s^{-1}),[15] respectively.

Results

Effect of Iodide Ions upon the Acidolysis Rate of $CrCMe_2OH^{2+}$. The possible effect of iodide ions on the acidolysis of $CrCMe_2OH^{2+}$ was examined since the iodide salts of 1-methylpyridinium and 1,4-dimethylpyridinium cations were used in the measurements. In the presence of up to 1.72×10^{-2} M I$^-$ (as KI) and $[CrCMe_2OH^{2+}]_0 = 3.0 \times 10^{-4}$ M, $[Cr^{2+}]_0 = 9.40 \times 10^{-3}$ M, and $[H^+] = 0.103$ M, the observed rate constants were within 6% of k_A and no noticeable effect

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(9) Abbreviations used in this paper: py, pyridine; 1-mpy, 1-methylpyridine; 4-mpy, 4-methylpyridine; dmpy, 1,4-dimethylpyridine; hpy, 3-hydroxypyridine; na, nicotinamide; ina, isonicotinamide.
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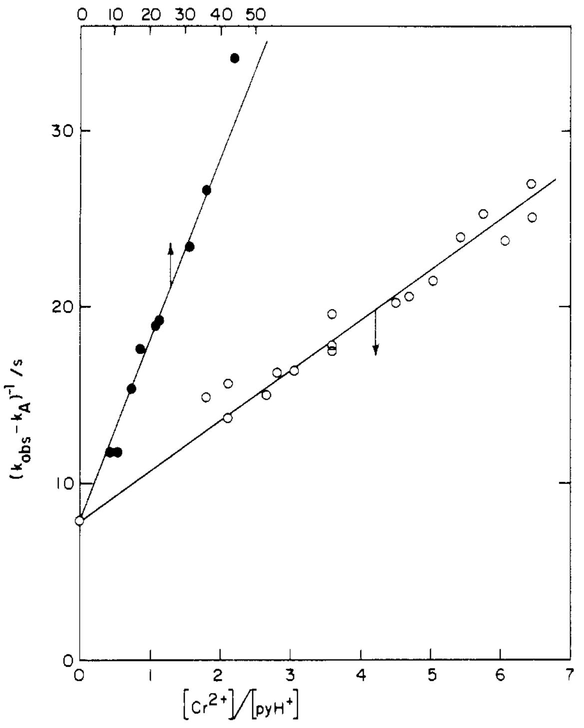


Figure 1. Linear dependence of $1/(k_{obsd} - k_A)$ on the concentration ratio. Data are shown for the 3-hydroxypyridinium ion (○) and for nicotinamide (●). The lines drawn are those resulting from the least-squares fit of the data to eq 3 using the known values of k_A, k_1, and k_{-1} (see text).

was observed. The concentrations of 1-methylpyridinium and 1,4-dimethylpyridinium iodides were maintained below 1.7 × 10^{-2} M for the kinetic measurements of these systems.

1-Methylpyridine, 3-Hydroxypyridine, and Isonicotinamide. The kinetic data[16] follow eq 3 precisely, as illustrated for 3-hydroxypyridine in Figure 1. The reaction rates are independent of $[H^+]$ in the range examined, ~0.01–0.2 M, implying that the pyridinium ion is the only important reacting species. The detailed kinetic data are available in the supplementary material[16] and are summarized in Table I. The rate constants were determined by using a nonlinear least-squares calculation according to eq 3, in which k_{obsd} was weighted by the inverse square of its value. The values of k_2 (dm^3 mol^{-1} s^{-1}) are 3.7 × 10^5 for 1-methylpyridinium ions, 1.4 × 10^8 for 3-hydroxypyridinium ions, and 1.2 × 10^9 for 4-(aminocarbonyl)pyridinium ions (protonated isonicotinamide).

1,4-Dimethylpyridine. This reaction is too slow to study by the present method. The observed rate constants are within 15% of the values of k_A even at the ratio of $[Cr^{2+}]/[1,4\text{-dimethylpyridine}] = 0.059$. On the basis of this ratio, the upper limit of the rate constant is ≤1 × 10^4 dm^3 mol^{-1} s^{-1}.

Nicotinamide. Upon addition of a nicotinamide solution to the solution of $CrCMe_2OH^{2+}$, the UV–visible spectrum showed the formation of an intermediate with an absorption maximum at 350 nm ($\epsilon \approx 1200$ dm^3 mol^{-1} cm^{-1} based on the initial concentration of $CrCMe_2OH^{2+}$). This intermediate species slowly decays in a complicated manner.

The formation of the intermediate was much faster than its subsequent decay, and the first step could be measured separately from the subsequent ones. The first step obeyed first-order kinetics and the observed rate constants obeyed eq 3, as also illustrated in Figure 1. The value of k_2 thus determined is 7.9 × 10^8 dm^3 mol^{-1} s^{-1}, and no dependence on $[H^+]$ was observed.

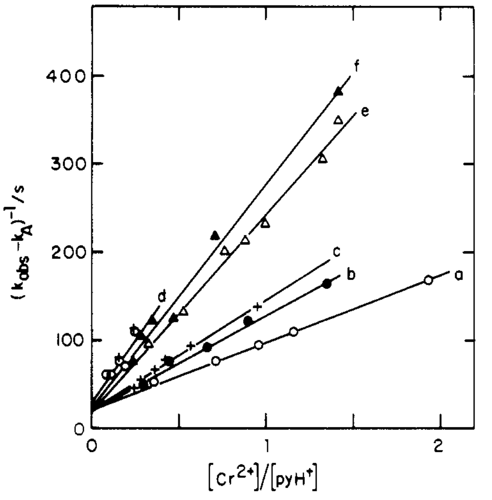
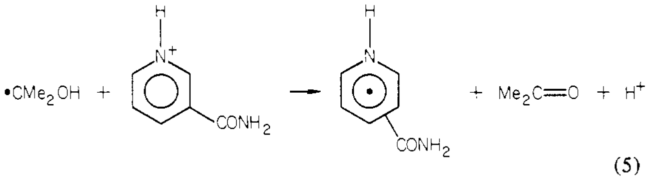


Figure 2. Linear plots of $1/(k_{obsd} - k_A)$ with the concentration ratio at fixed values of $[H^+]$ and $[Cr^{2+}]$ for the pyridinium ion. Values of $[H^+]$: 0.0120 (a), 0.0151 (b), 0.0245 (c), 0.103 (e), and 0.259 M (f), all at $[Cr^{2+}] = 9.40 \times 10^{-3}$ M; 0.0979 M (d), at $[Cr^{2+}] = 4.40 \times 10^{-3}$ M.

The intermediate species might be a nicotinamide–chromium complex formed by the sequence shown in eq 5 and 6.



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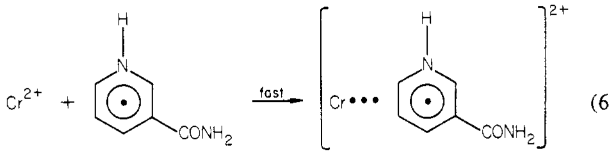

(6)

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The slow steps may be attributed to the decomposition of I, but they were not investigated in further detail.

Pyridine and 4-Methylpyridine. The kinetic data[16] did not conform to eq 3 but instead showed an additional dependence on $[Cr^{2+}]$ and a dependence on $[H^+]$. The data,[16] over a considerable range of concentration variation, did fit a modified expression. If eq 3 is rewritten with k_{app} in place of k_2, then at each $[H^+]$ the plot suggested by eq 4 yields a value of k_{app} that depends upon $[Cr^{2+}]$ and $[H^+]$ according to eq 7, as

$$k_{app} = k_2 + k'[Cr^{2+}]/[H^+] \qquad (7)$$

illustrated in Figure 2. As before, k_2 is the second-order rate constant for the reaction between $\cdot CMe_2OH$ and pyH^+ (eq 2); values are given in Table I. The second term in eq 7 signifies the reduction of a very low concentration of a chromium(II)–pyridine complex as detailed in the Interpretation and Discussion.

Interpretation and Discussion

Mechanism of Reduction of the Pyridinium Ions. The rate constants for all of these reactions are summarized in Table I. The agreement between our results and the published pulse-radiolytic values[5,6] for nicotinamide and isonicotinamide, cited in that table, provides substantiation of the present procedure.

The substituent group on the pyridine ring affects the reaction rate very appreciably. The rate constants for the 3- or 4-substituted pyridinium ions are correlated with Hammett

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(16) Tables of kinetic data for each reaction are given in the supplementary material.

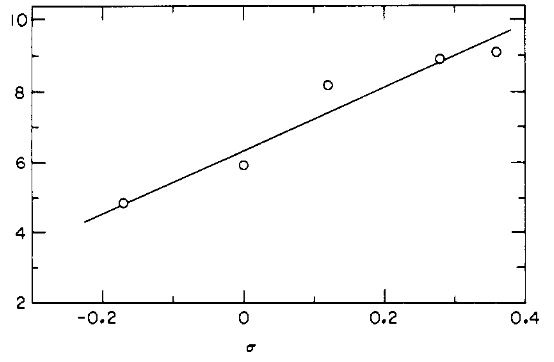
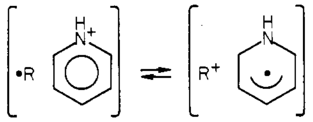


Figure 3. Correlation of the rate constants with the Hammett substituent parameter σ.

substituent constants $(\sigma)^{17}$ as shown in Figure 3. The positive value of ρ (+8.5) is consistent with the nucleophilic attack of the reducing radical, $\cdot CMe_2OH$, on the pyridines.

In many reactions between carbon-centered radicals and N-heterocyclic compounds, the aromatic ring is alkylated. The homolytic alkylation by nucleophilic radicals has been explained by a mechanism involving an activated complex similar to a charge-transfer complex (eq 8).[2] In the case of $\cdot CMe_2OH$



(8)

radicals, complete charge separation (electron transfer) occurs, and the alkylation of pyridines does not take place.[18] Since the covalent interaction is not developed in the transition state, the whole electron deficiency of the pyridine ring is the controlling factor of the reaction rates.[2] A good Hammett correlation with a positive ρ and no specific positional effect of the substituents is in agreement with the charge-transfer-like transition state.

Although the data for the N-methylated compounds are more limited, the rate decrease by a factor of ≥37 from $C_5H_5NCH_3^+$ to $4\text{-}CH_3C_5H_4NCH_3^+$ is quite comparable to the factor of 58 separating their parent ions.

Proposed Reduction of Chromium(II)–Pyridine Complexes. The two most slowly reacting pyridinium ions give evidence of an additional kinetic term, which may be expressed as $k'[\cdot C(CH_3)_2OH][pyH^+][Cr^{2+}][H^+]^{-1}$. This rate law term is consistent with a parallel pathway in which the free radical reduces a Cr(II)–pyridine complex in labile equilibrium with the reactants (eq 9 and 10). Provided only a small fraction

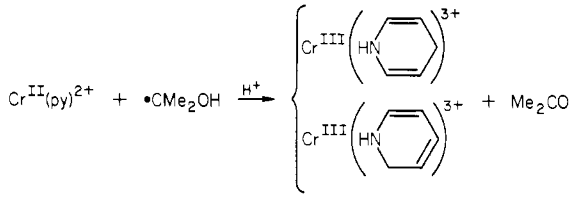
$$Cr^{2+}(aq) + pyH^+ \overset{K_9}{\rightleftharpoons} Cr(py)^{2+} + H^+ \qquad (9)$$

$$Cr(py)^{2+} + \cdot C(CH_3)_2OH \xrightarrow{k_{10}} Cr(py)^+ + (CH_3)_2CO + H^+ \qquad (10)$$

of the reactant is present as $Cr(py)^{2+}$ (an assumption that seems quite reasonable considering the values of K_9 for other divalent first-row metal ions[19]), the mechanism of eq 9 and 10 leads to the rate law term identical with that found experimentally, such that $k' = K_9k_{10}$. The values are 4.1×10^6 $M^{-1}\ s^{-1}$ ($C_5H_5NH^+$) and 2.5×10^5 $M^{-1}\ s^{-1}$ ($4\text{-}CH_3C_5H_4NH^+$).

Since K_9 is not known, the true bimolecular rate constant cannot be calculated. On the other hand, the stability constant K' for the equilibrium $M^{2+} + py \rightleftharpoons Mpy^{2+}$ lies generally in the range 10–100 M^{-1}.[19] The value of K_9 is given by $K_9 = K'K_a$, where K_a is the acid ionization constant of pyH^+ ($K_a = 6.17 \times 10^{-6}$ and 5.50×10^{-7} M for $C_5H_5NH^+$ and $4\text{-}CH_3C_5H_4NH^+$, respectively). On that basis approximate values of k_{10} are 10^9–10^{10} $M^{-1}\ s^{-1}$ for the two species.

Experiments in which Zn^{2+} was added (in addition to the amount present in the Cr^{2+} solutions) gave the same rate constants, indicating that a kinetic term in which $Zn(py)^{2+}$ oxidizes $\cdot C(CH_3)_2OH$ is not important. This suggests that the role of Cr^{2+} in eq 10 is not simply to increase the electron affinity of pyridine by virtue of its positive charge. Rather, it suggests an appreciable reactivity of the pyridine by coordination to Cr(II). A possible mechanism is presented in eq 11. The pyridine is partly reduced by coordination to Cr^{2+}



(11)

and accessible to one more electron to form a stable nonradical species (dihydropyridine). The product analysis supports this mechanism. The product solution was subjected to the SP-Sephadex C-25 (Na^+ form) cation-exchange column, and a reddish violet band was found ahead of the Cr^{3+} band. The yield of the reddish violet species was 12–14% of the initial concentrations of $CrCMe_2OH^{2+}$ under the conditions $[H^+] = 0.07$–0.1 M, $[Cr^{2+}]_0 = (3.5\text{–}6.9) \times 10^{-3}$ M, and $[pyH^+]_0 = 0.064$–0.1 M. This yield corresponds approximately to the k_{10} pathway. The visible absorption spectrum slightly changed depending on the reactant concentrations, which indicated that the reddish violet band was a mixture of similar species. Absorption maxima were found at 533–542 nm ($\epsilon = 23$–32 $M^{-1}\ cm^{-1}$) and 400–410 nm ($\epsilon = 24$–31 $M^{-1}\ cm^{-1}$). The spectrum is different from that of the (pyridine)pentaaquachromium(III) ion (λ_{max} ($\epsilon/M^{-1}\ cm^{-1}$) = 560 nm (18.2), 402 nm (20.8))[20] but similar to that of amminepentaaquachromium(III) (545 nm (22.1), 397 nm (21.8)).[21] These results support the product formulations shown in eq 11.

A corresponding kinetic term was not found for the other pyridinium ions, all of which are either *N*-methyl derivatives (and hence unable to complex chromium(II)) or else compounds that react very rapidly by the k_2 pathway. Even if k_{10} approaches the diffusion-controlled limit, as it appears to do, the pathway represented by eq 9 and 10 could not be appreciable in comparison to the higher values of k_2.

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.

Registry No. $4\text{-}CH_3C_5H_4NCH_3^+$, 18241-35-5; $4\text{-}CH_3C_5H_4NH^+$, 16950-21-3; $C_5H_5NCH_3^+$, 694-36-4; $C_5H_5NH^+$, 16969-45-2; $3\text{-}OHC_5H_4NH^+$, 33825-36-4; $3\text{-}(CONH_2)C_5H_4NH^+$, 38719-50-5; $4\text{-}(CONH_2)C_5H_4NH^+$, 40617-90-1; $\cdot CMe_2OH$, 5131-95-3; $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3.

Supplementary Material Available: Tables of kinetic data for each reaction (6 pages). Ordering information is given on any current masthead page.

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