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Kinetics and Mechanisms of the Reductions of Three Isomeric μ-Pyridinecarboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] Complexes by Chromium(II) and Vanadium(II)

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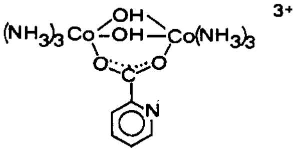
The kinetics of the reductions of three isomeric μ-pyridinecarboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes by $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ have been studied in perchloric acid media. Reduction of the first Co(III) is rate determining in all cases. The Cr(II) reductions of μ-pyridine-2-carboxylato and μ-pyridine-4-carboxylato complexes are dependent on H^+ concentration according to the rate law $-d \ln [Co^{III}_2]/dt = k[Cr^{2+}]/[H^+]$. This is consistent with an inner-sphere mechanism with attack of Cr(II) at the deprotonated remote pyridine nitrogen atom: $k = k_{Cr}K_a$, where K_a is the acid dissociation constant. Specific rate constants, k_{Cr} (M^{-1} s^{-1}), at 25 °C and ionic strength $\mu = 0.5$ M ($LiClO_4$), enthalpies (kcal mol^{-1}), and entropies (cal K^{-1} mol^{-1}) of activation are, for the μ-pyridine-2-carboxylato complex, 15.1 ± 1.5, 11.4 ± 1.0, and −19.6 ± 3.0 and, for the μ-pyridine-4-carboxylato isomer, 110 ± 10, 5.7 ± 0.8, and −33.5 ± 3.0. Reductions of both complexes by V(II) are independent of $[H^+]$ and occur via an outer-sphere mechanism. The μ-pyridine-3-carboxylato complex is reduced independently of $[H^+]$ in the range of 0.5–0.05 M perchloric acid by Cr(II) and V(II) following the simple rate law $-d \ln [Co^{III}_2]/dt = k_{Red}[\text{reductant}]$. Rate constants ($M^{-1}$ s^{-1}) at 25 °C and $\mu = 1.0$ M ($LiClO_4$) are $k_{Cr} = (3.26 \pm 0.04) \times 10^{-3}$ and $k_V = 0.154 \pm 0.007$. Outer-sphere mechanisms for both reactions are assigned on the basis of a k_{Cr}/k_V ratio of 0.021. The Cr(II) reduction of the mononuclear pyridine-4-carboxylatopentaamminecobalt(III) complex has been reinvestigated. Activation parameters have been determined. The observed rate patterns are discussed in terms of differing reducibilities of the uncomplexed ligands by Cr(II) and varying basicities of the pyridine nitrogen atoms going from mononuclear to binuclear Co(III) complexes.

Introduction

The advantages of binuclear cobalt(III)–ammine complexes with carboxylato bridging ligands for mechanistic studies on electron-transfer reactions through organic structural units using $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ ions as reductants are now well established.[1-3] Reduction of the first Co(III) center is of the inner-sphere type if the organic ligand bears a second functional group and an "electron mediating" structural unit between these groups. Thus it is possible to study inner-sphere reductions with remote attack of the reductant and transfer of an electron through the ligand. The complications of parallel inner-sphere reactions observed for the reductions of carboxylatopentaamminecobalt(III) complexes with attack of the reductant at the adjacent uncomplexed carbonyl oxygen atom are avoided.

The present study is concerned with electron-transfer reactions through the nitrogen atom of three isomeric pyridinecarboxylic acids. It was of interest to study possible inner-sphere type reductions of the binuclear complexes I–III with expected simple attack of the reducing agents Cr(II) and V(II) at the remote pyridine nitrogens as compared to the more complicated reactivity pattern of the mononuclear $(NH_3)_5Co$ analogues.[4]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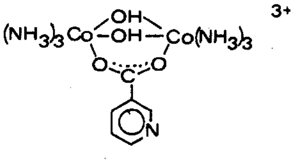
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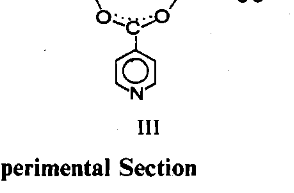
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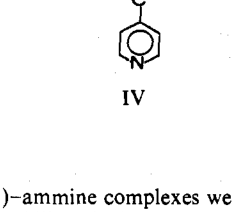

IV

Experimental Section

Complexes. The binuclear cobalt(III)–ammine complexes were prepared as described previously.[5] The stability of all complexes in solution was checked spectrophotometrically. No spectral changes of complex solutions ($[H^+] = 1.0$ and 0.1 M) were detected for at least 24 h at 30 °C. The mononuclear pyridinecarboxylatopentaamminecobalt(III) complexes were prepared from aquopentaamminecobalt(III) perchlorate and the organic ligand in water as described in the literature.[4] The complexes gave peaks at 502 nm (ε 79 l. mol^{-1} cm^{-1}) in good agreement with previous values.

Reagents. Solutions of $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ ions in perchloric acid were prepared by electrolytic reduction of chromium(III) and vanadium(IV) solutions under an argon atmosphere. Lithium perchlorate was obtained from Li_2CO_3 and concentrated $HClO_4$ and was purified by recrystallization. The organic ligands were commercially available and were used without further purification.

Ion-Exchange Separations. Dowex 50W-X8 exchange resin in the hydrogen and lithium form was used. Additional separations were carried out using Sephadex SP C-25 (H^+ and Li^+ form). Chromium and cobalt(II) concentrations were determined spectrophotometrically as chromate and as an intensively colored complex with 2-hydroxy-1-nitroso-3,6-naphthalenedisulfonic acid, respectively.[6]

Kinetic Measurements. The Cr(II) and V(II) reductions were followed on a Unicam SP 1700B spectrophotometer at the first absorption maximum of the binuclear complexes (λ_{max} 524 nm, ε 110 l. mol^{-1} cm^{-1}) and at 502 nm for the mononuclear complexes (ε ~80). The reaction mixtures were thermostated by an external temperature bath (±0.1 °C). The reductions were carried out in cells fitted with rubber serum caps through which the reductant was added with a hypodermic syringe. To ensure complete mixing of reactants a rapid stream of argon was passed through the solution for 5 s. All reactions were carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. The reactions were followed for 6–7 half-lives. First-order rate constants were evaluated graphically from gradients (×2.303) of plots of log ($OD_t - OD_\infty$) against time, where OD_t is the absorbance at time t and OD_∞ that after reaction is complete. The plots were linear to better than 90% completion of the reaction in all cases.

Determination of Dissociation Constants. All complexes of the present series have a basic pyridine nitrogen atom which can protonate in aqueous acidic solution. Apparent pK_a values of complexes at 0.5 M ionic strength ($LiClO_4$) were evaluated spectrophotometrically.[7] The largest differences in spectra were observed at 270 nm for the pyridine-4-carboxylato complexes (mononuclear and binuclear) and the pyridine-2-carboxylato complex (I). In this region spectra of the uncomplexed ligands show changes as a function of hydrogen ion concentration. Since the actual differences of spectra of the fully protonated and deprotonated species of the complexes were relatively small, determinations of extinction coefficients as a function of pH were not very accurate and large error limits are attached (Table III).

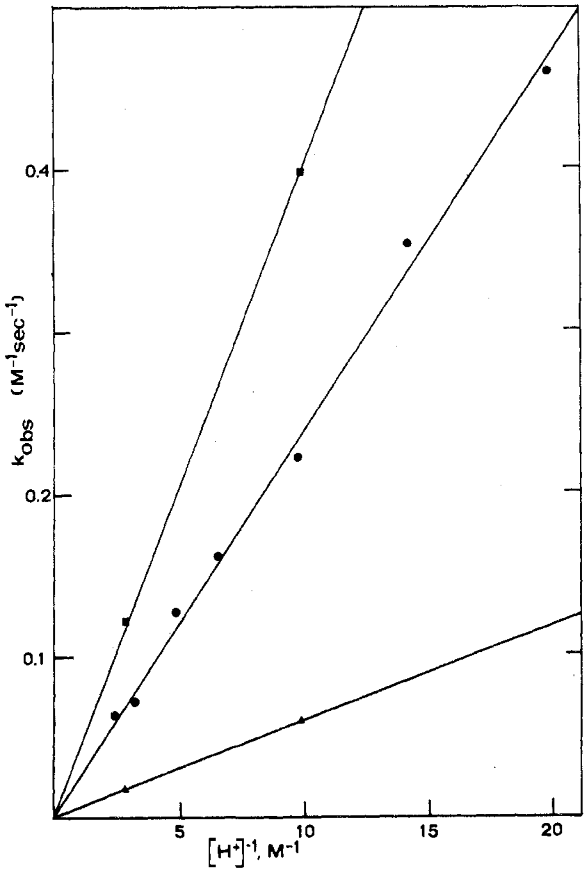


Figure 1. Dependence of the reduction rate of μ-pyridine-2-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] by chromium(II) on $[H^+]^{-1}$ (μ = 0.5 M (LiClO$_4$)): ▲, 5 °C; ●, 25 °C; ■, 35 °C.

Table II. Summary of Kinetic Parameters for the Reductions of Pyridinecarboxylatocobalt(III)-Ammine Complexes by Chromium(II) at 25 °C

Complex	k_{Cr}, M^{-1} s^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, K^{-1} mol^{-1}	Mechanism[e]
I[a]	15.1 ± 1.5[c]	11.4 ± 1.0	−19.6 ± 3.0	i.s. remote attack
II[b]	(3.26 ± 0.04) × 10^{-3}			o.s.
III[a]	110 ± 10[c]	5.7 ± 1.0	−33.5 ± 3.0	i.s. remote attack
IV[a]	835 ± 100[c]	5.0 ± 1.0	−32.0 ± 3.0	i.s. remote attack
	0.87 ± 0.004[d]	4.1 ± 0.2	−45.0 ± 1.0	i.s. adjacent attack

[a] μ = 0.5 M (LiClO$_4$). [b] μ = 1.0 M (LiClO$_4$). [c] Error limits are predominantly due to large uncertainties of spectrophotometrically determined values of K_a (Table III). [d] Acid-independent path k_0. [e] i.s. = inner-sphere; o.s. = outer-sphere.

Table III. Dissociation Constants and Thermodynamic Parameters of Complexes I-IV

Complex	T, °C	pK_a	ΔH_0, kcal mol^{-1}	ΔS_0, cal K^{-1} mol^{-1}
		A. Potentiometric Determinations		
I	5.0	1.98 ± 0.01	−0.85 ± 0.3	−12.1 ± 2.0
	25.0	2.03 ± 0.01		
	35.0	2.045 ± 0.01		
II	25.0	2.79 ± 0.01		
III	5.0	3.24 ± 0.01	+1.6 ± 0.6	−9.1 ± 2.0
	25.0	3.16 ± 0.01		
	35.0	3.12 ± 0.01		
IV	10.5	4.15 ± 0.01	+2.92 ± 0.5	−8.7 ± 2.0
	25.5	4.04 ± 0.01		
	42.0	3.92 ± 0.01		
		B. Spectrophotometric Determinations at Ionic Strength 0.5 M (LiClO$_4$) and 25.0 °C		
I		2.83 ± 0.05		
III		3.90 ± 0.05		
IV		4.74 ± 0.05		

Mainly due to this behavior measurements at 35 and 5 °C did not reveal reproducible dependencies of pK_a values on the temperature. In order to determine activation parameters for the reduction of the present Co(III) complexes by Cr(II) it was necessary to evaluate the thermodynamic parameters ΔH_0 and ΔS_0 for the protonation equilibria. Therefore, acid dissociation constants for all complexes were measured potentiometrically by titrating 0.01 M complex solutions with 0.1 M NaOH at three different temperatures.[7] This method yields more precise values with considerably smaller error limits.

Results

Reduction of the μ-Pyridine-2-carboxylato Complex (I) by Cr(II). The stoichiometry of the reduction of complex I by Cr(II) was shown to be 2:1 from ion-exchange experiments as in (1). The reduction of the binuclear complex was strongly

$$2Cr^{2+} + Co^{III}{}_2 \rightarrow 2Cr(III) + 2Co^{2+} \qquad (1)$$

dependent on hydrogen ion concentration and followed the rate law (2). The rate data are given in Table I (supplementary

$$-d \ln [Co^{III}{}_2]/dt = k[Cr^{2+}]/[H^+] = k_{obsd}[Cr^{2+}] \qquad (2)$$

material). The acid dependence of k_{obsd} is illustrated in Figure 1 and the kinetic parameters are summarized in Table II. One rate-determining step is observed during which time both Co(III) ions are reduced. This is consistent with a form of complex(I) deprotonated at the pyridine nitrogen being the reactant. Thus eq 3 can be derived, where K_a is the disso-

$$k_{obsd} = k_{Cr}K_a/(K_a + [H^+]) \qquad (3)$$

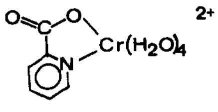
ciation constant of the protonation equilibrium and k_{Cr} the second-order rate constant for the reduction of the deprotonated form of I by Cr(II), and since $K_a << [H^+]$ eq 3 reduces to eq 4. k_{Cr} at 25 °C was obtained from the gradient

$$k_{obsd} = k_{Cr}K_a/[H^+] \qquad (4)$$

in Figure 1 and the spectrophotometrically determined dissociation constant (Table III). Apparent activation parameters $\Delta H_a^‡$ and $\Delta S_a^‡$ were calculated from the slopes in Figure 1 using an unweighted nonlinear least-squares program.[8] The values obtained are composite and were corrected for thermodynamic parameters (Table III) of the protonation equilibrium as in (5). The reaction products were determined

$$\Delta H^‡ = \Delta H_a{}^‡ - \Delta H_0$$
$$\Delta S^‡ = \Delta S_a{}^‡ - \Delta S_0 \qquad (5)$$

by allowing a solution of $[Cr^{2+}]$ = 0.0112 M, $[Co^{III}{}_2]$ = 0.5 × 10^{-2} M, and $[H^+]$ = 0.10 M to react for 45 min at 25°, after which time no further uv-visible spectrophotometric changes were observed. The solution was then air oxidized to remove excess Cr(II). The products were separated by ion-exchange chromatography and gave the following products expressed as percentages of the total Co(III) reactant: $[Co(H_2O)_6]^{2+}$ (96%), a pink-violet chromium(III)-containing complex (43%) which was eluted off the column directly after $[Co(H_2O)_6]^{2+}$ with an apparent 2+ charge, $[Cr(H_2O)_6]^{3+}$ (58%), and a green band containing dimeric and trimeric Cr(III) species generated by air oxidizing of excess Cr(II) with a charge >3+ which was not removed from the column. The visible spectrum of the pink-violet chromium(III) complex with a 2+ charge had maxima (extinction coefficient) at 535 nm (42.1 l. mol^{-1} cm^{-1}) and 403 nm (43.7). Color and charge of this complex suggest a chelated structure V. The same complex is the only Cr(III) product when monomeric pyridine-2-carboxylatopentaamminecobalt(III) reacts with Cr(II)[4] but the reported spectrum (λ_{max} 553 (32.8) and 406 (50.8)) is not in agreement with our data. Therefore, it was felt that a brief reinvestigation of the reaction was appropriate using ion-exchange techniques which had not been done previously. From 1:1 reaction mixtures only two fractions containing pink $[Co(H_2O)_6]^{2+}$ and the desired pink-violet Cr(III) species were eluted off the column with 0.2 M $HClO_4$ in that order. The visible spectrum of this Cr(III) complex had maxima at 536 nm (44.9) and 403 nm (44.0). This is in good agreement with our results. It is concluded that the pink-violet Cr(III) products with a 2+ charge obtained from the reduction of monomeric and binuclear Co(III) complexes with pyridine-2-carboxylic acid as ligands are identical (structure V).



V

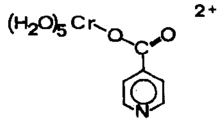
Reduction of the μ-Pyridine-3-carboxylato Complex (II) by Cr(II). The stoichiometry of the reaction was found to be 2:1 as in eq 1. The reduction of the μ-pyridine-3-carboxylato isomer by Cr(II) was independent of hydrogen ion concentration in the range of 0.5–0.05 M perchloric acid and followed the simple rate law (6). Reduction of the first Co(III) center

$$-d \ln [Co^{III}{}_2]/dt = k_{Cr}[Cr^{2+}] \qquad (6)$$

is slow and rate determining. Rate data at 25 °C are given in Table I. Because of the slowness of the overall reaction and subsequent reactions which reaction products might undergo, ion-exchange separation of primary chromium(III) products was not feasible.

Reduction of the μ-Pyridine-4-carboxylato Complex (III) by Cr(II). The stoichiometry of the reduction of complex III by Cr(II) was as in (1). The reaction was strongly dependent of hydrogen ion concentration and followed the rate law (2). The rate data are given in Table I. A plot k_{obsd} vs. $[H^+]$ is shown in Figure 2. Again reduction of the first Co(III) is rate determining. The kinetic behavior is very similar to the reduction of the μ-pyridine-2-carboxylato derivative. The deprotonated form of complex III is the reactant and eq 3 and 4 can be applied. The activation parameters were determined as described for the reduction of complex I by Cr(II). The kinetic parameters are summarized in Table II.

Attempts to separate and characterize the various chromium(III) products by ion-exchange methods were not successful. Reaction mixtures with low (0.05 M) and high (1.0 M) hydrogen ion concentrations and a Cr(II) to complex ratio of 2:1 yielded one blue Cr(III)-containing fraction which was eluted off the column after pink $[Co(H_2O)_6]^{2+}$. This behavior appeared to be independent of the ion-exchange resin used (Sephadex SP C-25, Dowex 50W-X8 in the H^+ or Li^+ form, respectively). The spectrum of this blue product had maxima (extinction coefficient) at 409 nm (21.8) cm^{-1}) and 574 nm (21.1). The positions of the maxima are in agreement with those reported for $[Cr(H_2O)_6]^{3+}$ but the extinction coefficients are too "high". Reduction of the mononuclear pyridine-4-carboxylatopentaamminecobalt(III) complex by Cr(II) is believed to yield VI as the sole product. A product analysis by ion exchange techniques of this reaction was carried out. Separation of a 1:1 reaction mixture gave two fractions: pink $[Co(H_2O)_6]^{2+}$ and a blue Cr(III)-containing fraction. The latter had maxima at 408 nm (ϵ 22.6 l) and 572 nm (ϵ 22.1) which agree reasonably well with those reported previously.[4] A portion of this fraction was mixed with a known amount of $[Cr(H_2O)_6]^{3+}$ in perchloric acid. The solution was then charged onto an ion-exchange column (using Dowex and Sephadex resins). Elution with various $LiClO_4$–$HClO_4$ solutions did not separate the different Cr(III) species. Since it has not been possible to separate $[Cr(H_2O)_6]^{3+}$ from other Cr(III) species carrying the organic ligand it is concluded that the blue Cr(III)-containing fraction obtained from reaction of complex III with Cr(II) is in fact a mixture of $[Cr(H_2O)_6]^{3+}$ and possibly complex VI. The stoichiometry of this reaction is in support of this interpretation because it is not possible to produce only one uniform Cr(III) species (other than hexaaquochromium(III)) with a 2+ or 3+ charge (Scheme II). It should be noted that the reaction of the mononuclear pyridine-4-carboxylato complex IV with Cr(II) may also yield only a mixture of hexaaquochromium(III) and complex VI.



VI

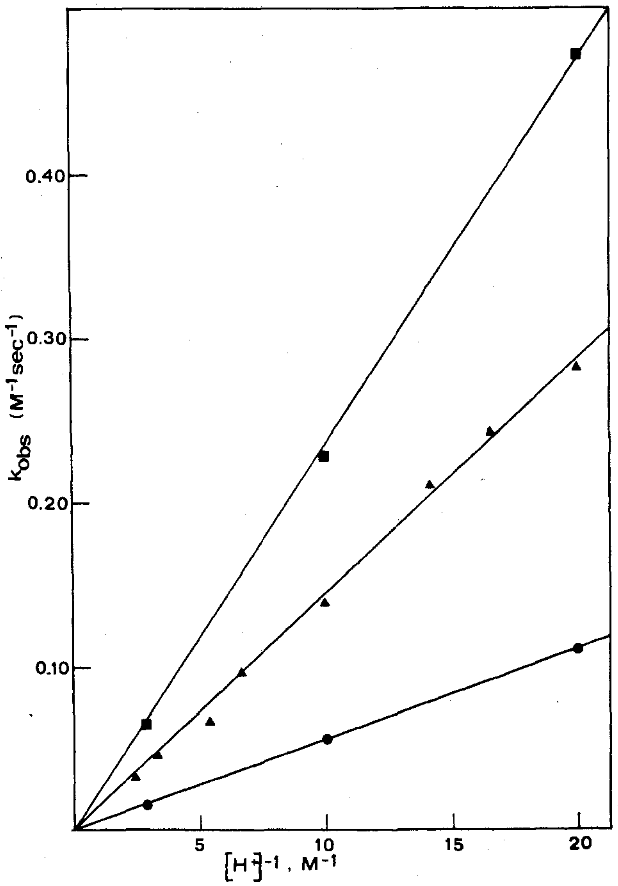
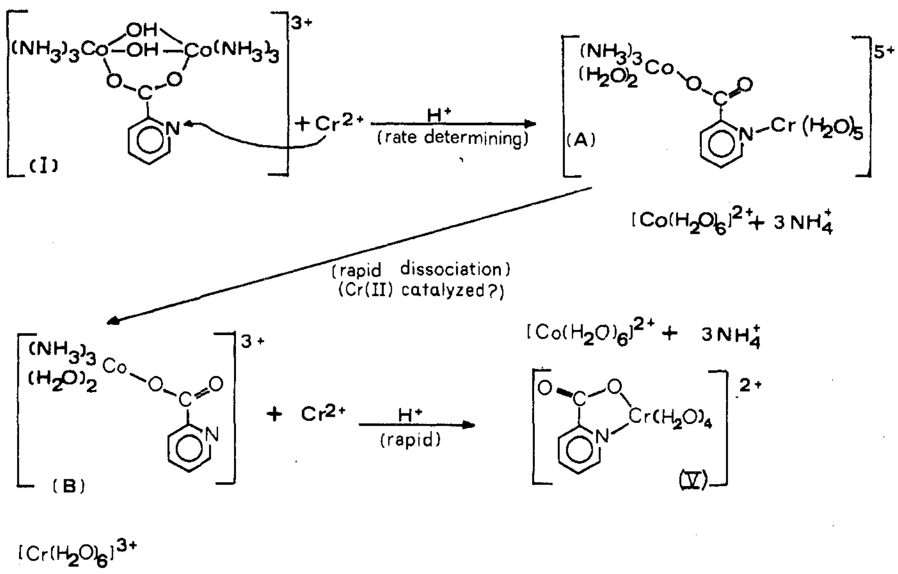


Figure 2. Dependence of the reduction rate of μ-pyridine-4-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] by chromium(II) on $[H^+]^{-1}$ (μ = 0.5 M ($LiClO_4$)): ●, 5 °C; ▲, 25 °C; ■, 35 °C.

Reduction of the Mononuclear Pyridine-4-carboxylatopentaamminecobalt(III) Complex by Cr(II). It was of interest to determine the influence of *two* coordinated Co(III) centers bonded to the carboxylic group on the rate of reduction and on the basicity of the remote pyridine nitrogen atom as compared to only *one* coordinated Co(III). The Cr(II) reduction of the mononuclear complex IV has been studied previously at 25 °C and an ionic strength of 3.0 M using $NaClO_4$ as supporting electrolyte.[4] A brief reinvestigation of this reaction has been carried out at an ionic strength of 0.5 M ($LiClO_4$) in order to determine activation parameters.

Scheme I



The reaction is dependent of [H+] and follows the rate law (7) as reported previously; K_a is the dissociation constant of

$$-\mathrm{d}\ln[\mathrm{Co^{III}}]/\mathrm{d}t = (k_0 + k_1K_a/[\mathrm{H^+}])[\mathrm{Cr^{2+}}] \qquad (7)$$

complex IV. The rate data are given in Table I. The dependence of the reaction on [H+] is shown in Figure 3 and the kinetic parameters are summarized in Table II. Comments on possible reaction products were made in the preceding section.

Reductions of the Binuclear μ-Pyridinecarboxylato Complexes I–III by V(II). The reductions of complexes I–III by V(II) have been studied at 25 °C and were found to be independent of H^+ concentration. Absorbance changes at 850 nm ($[V(H_2O)_6]^{2+}$ peak, ϵ 3.22 l. mol^{-1} cm^{-1}) for solutions containing ca. tenfold excess of V(II) were consistent with 2:1 stoichiometries as in (8). Reduction of the first Co(III) is

$$2V^{2+} + \mathrm{Co^{III}}_2 \rightarrow 2V(III) + 2Co^{2+} \qquad (8)$$

rate determining. A strictly first-order dependence on reductant was observed (eq 9). The rate data and second-order

$$-\mathrm{d}\ln[\mathrm{Co^{III}}_2]/\mathrm{d}t = k_V[V^{2+}] \qquad (9)$$

rate constants at 25 °C are listed in Table IV.

Discussion

The observed rate law and the product analysis for the reduction of the binuclear μ-pyridine-2-carboxylato complex (I) are consistent with an inner-sphere mechanism. The first Co(III) is reduced with remote attack of the reducing agent at the deprotonated pyridine nitrogen atom. A binuclear Co(III)–Cr(III) intermediate A is generated. (See Scheme I.) This intermediate does not survive because of the lability of the Cr–N bond and decomposes to give $[Cr(H_2O)_6]^{3+}$ and intermediate B which is rapidly reduced by a second Cr(II) via an inner-sphere mechanism with adjacent attack with chelation of the reductant. The Cr(III) product of this step is a chelated complex (V). It is conceivable that at low [H+] a small portion of B is reduced via the aquo ligands, thereby producing $[Cr(H_2O)_6]^{3+}$. This may account for the observed product ratio of $[Cr(H_2O)_6]^{3+}$ to complex V of 58:42 and not 50:50 as is implied by Scheme I. Reduction of the first Co(III) center by adjacent attack with chelation of Cr(II) is not considered an alternative interpretation. It has been pointed out that carbonyl oxygen atoms coordinated to Co(III) do not represent easily accessible sites for additional coordination to Cr(II) which would be a necessary prerequisite for an adjacent attack with chelation mechanism.[15] The rate of reduction of the mononuclear analogue, pyridine-2-carboxylatopentaamminecobalt(III), is faster by 4 orders of magnitude.[4] In contrast the rates of reduction of binuclear complex I and complex III where an adjacent attack with chelation mechanism is excluded on steric grounds are quite similar. This

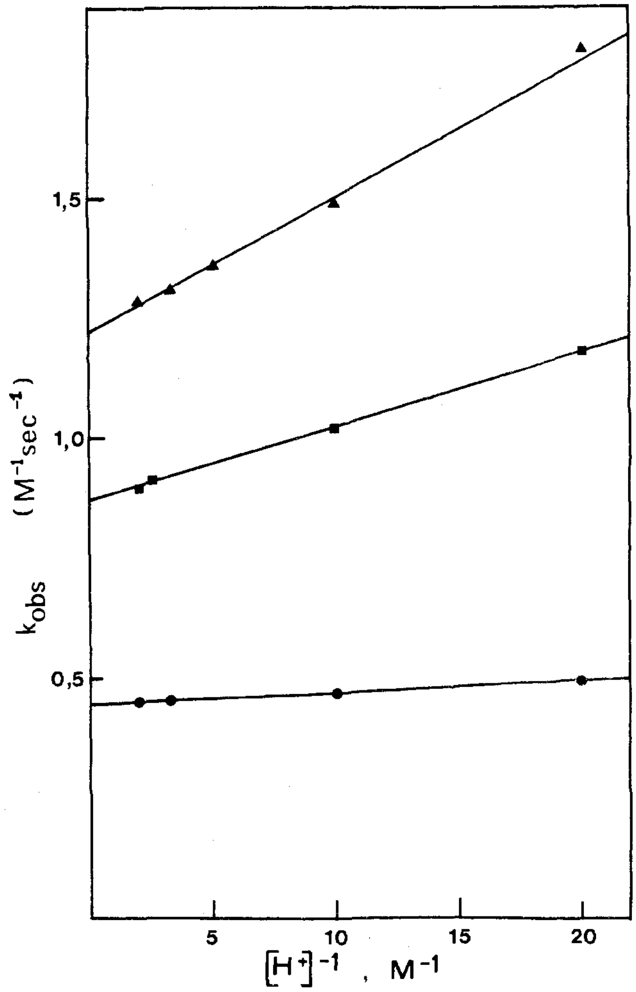


Figure 3. Dependence of the reduction rate of pyridine-4-carboxylatopentaamminecobalt(III) by chromium(II) on $[H^+]^{-1}$ (μ = 0.5 M (LiClO$_4$)): ●, 2 °C; ■, 25 °C; ▲, 39.4 °C.

Scheme II

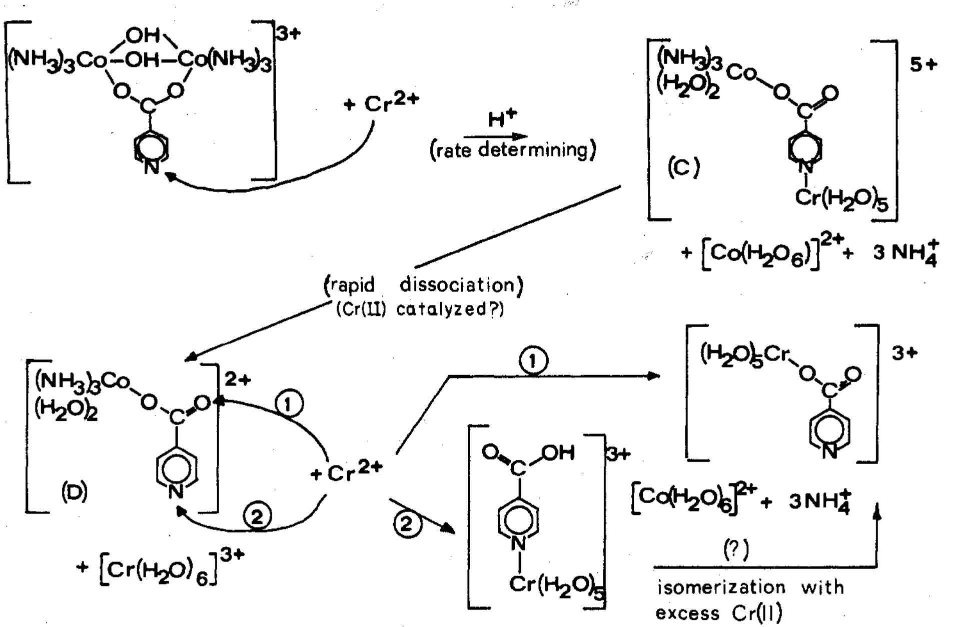


Table IV. Kinetic Data for the Reductions of Binuclear, Isomeric μ-Pyridinecarboxylato Complexes I-III by Vanadium(II) at 25 °C

Complex	$[H^+]$, M	10^2-$[V^{2}]$, M	10^3-$[Co^{III}_2]$, M	k_V, M^{-1} s^{-1}
I[a]	0.05	0.96	0.5	0.352
	0.09	4.89	1.0	0.358
	0.15	2.36	1.0	0.350
	0.15	5.71	2.0	0.359
	0.25	7.50	1.0	0.351
	0.40	2.56	1.0	0.355
	0.40	3.50	0.5	0.361
				Av 0.355 ± 0.005
II[b]	0.05	1.64	0.5	0.156
	0.50	5.37	0.5	0.145
	0.50	7.16	1.0	0.154
	0.50	9.01	1.0	0.160
				Av 0.154 ± 0.007
III[a]	0.03	0.71	0.5	0.155
	0.09	2.03	0.5	0.158
	0.10	3.42	1.0	0.155
	0.21	4.62	1.0	0.157
	0.30	6.31	2.0	0.157
	0.30	2.01	0.5	0.156
				Av 0.156 ± 0.001

[a] $\mu = 0.5$ M ($LiClO_4$). [b] $\mu = 1.0$ M ($LiClO_4$).

indicates that an identical mechanism is operative (inner sphere with remote attack at the pyridine nitrogen atoms).

Since the reduction by Cr(II) of the μ-pyridine-4-carboxylato complex III is dependent on acid concentration, attack of the reductant most likely takes place at the unprotonated pyridine nitrogen (inner-sphere mechanism with remote attack of Cr(II)). (See Scheme II.) The generated intermediate C decomposes to give $[Cr(H_2O)_6]^{3+}$ and a second intermediate D. According to the displayed hypothetic reaction scheme, D can be reduced either by adjacent attack at the carbonyl oxygen or by remote attack at the pyridine nitrogen. The Cr(III) product obtained by the second step of the reaction would be complex VI. This scheme predicts a 50:50 reaction mixture of hexaaquochromium and complex VI. The only experimental data concerning the actual product distribution have been summerized above. They do not allow a more detailed description of the second step of the reaction.

Inner-sphere reduction of the mononuclear complex IV takes place by attack of Cr(II) at the adjacent carbonyl oxygen atom and at the deprotonated remote pyridine nitrogen.[4] The rates of reduction at an ionic strength of 0.5 M ($LiClO_4$) are somewhat retarded as compared to those at 3.0 M. This is in accord with two positively charged species reacting. Taube and Gould have pointed out that the rate of the $[H^+]$-independent path k_0 is enhanced compared to "normal" rates for an inner-sphere adjacent attack mechanism—possibly due to conjugative stabilization of an intermediate radical ion by the pyridine ring.[4] (The rate constant of the reduction of the sterically equivalent benzoatopentaamminecobalt(III) complex[9] by Cr(II) at 25 °C is 0.15 M^{-1} s^{-1}, $\Delta H^{\ddagger} = 9.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = -32$ cal K^{-1} mol^{-1}). This observation is bolstered by a significantly smaller enthalpy of activation (4.1 kcal mol^{-1}) for the k_0 path of the reduction of complex IV (Table II). On the other hand, it is noted that the entropy of activation appears to be more negative (−45 cal K^{-1} mol^{-1}). This can account for the fact that a 3+ species (the protonated form of complex IV) is reduced whereas the corresponding benzoato complex has a 2+ charge.

All of the evidence presented so far confirms that the deprotonated forms of complexes I, II, and IV react with Cr(II) by an inner-sphere mechanism with simple remote attack of the reductant at the basic pyridine nitrogen atom and transfer of one electron through the aromatic ring. Inspection of the kinetic parameters in Table II shows that although the mode of reduction of the first Co(III) is identical for all three reactions, the rate constants differ markedly.

Steric hindrance may account for the relatively small rate constant which is observed for the μ-pyridine-2-carboxylato complex I. Space-filling models indicate that formation of the trinuclear Co^{III}_2–Cr^{II} precursor complex requires a twisted conformation of complex I where the pyridine ring is approximately perpendicular to the carboxylic group. The basic nitrogen atom is now exposed and enables N–Cr^{II} bond making. Due to the noncoplanarity the conjugation is reduced and electron transfer through the bridging ligand may be impaired. It is noted that the enthalpy of activation is found to be nearly twice as big as is the case for the pyridine-4-carboxylato complexes.

Steric effects cannot explain the difference of rates which is observed for the reductions of the mononuclear and binuclear complexes III and IV by Cr(II). Complex IV is reduced approximately 1 order of magnitude faster than the corresponding binuclear complex III at 25 °C. The situation is even more intricate because an increasing oxidation potential for the Co(III)–Co(II) couple as the number of coordinated ammonia ligands decreases from 5 (mononuclear complex IV) to 3 (binuclear complex III)[10] would predict the reverse behavior.

However, the pK_a values (Table III) for the dissociation constants of complexes III and IV differ by an order of magnitude as well. If these pK_a values are taken as a measure of the basicity of the pyridine nitrogen atom, it turns out that the mononuclear complex IV has a more basic nitrogen atom as compared to complex III where two electron-withdrawing Co(III) centers influence the free pair of electrons at the pyridine nitrogen.

Since the reductions of these complexes by Cr(II) involve the formation of precursor complexes, the measured rates are a function of the precursor complex formation constant, K, and the intrinsic electron transfer rate constant, k_{et} (eq 10).

$$k_{\mathrm{Cr}} = k_{\mathrm{et}}K \qquad (10)$$

The varying precursor complex stabilities which are affected by differing basicities of the two pyridine nitrogen atoms offer a plausible explanation for the observed rate pattern, if K is assumed to be larger for the precursor complex formation with the more basic nitrogen atom, i.e., complex IV. The intrinsic rate constant, k_{et}, is assumed to be identical for both reactions. This implies a radical intermediate mechanism to be operative; the reducing electron is transferred from Cr(II) to produce the ligand radical which in turn reduces Co(III). The apparent independence of rates of the higher oxidation potential for the μ-pyridine-4-carboxylato complex III is in support of this interpretation.

The reduction of the μ-pyridine-3-carboxylato complex II by Cr(II) is independent of H^+ concentration. The observed rate constant at 25 °C is 1000 or 10000 times smaller than those for complexes I and III. The corresponding mononuclear pyridine-3-carboxylatopentaamminecobalt(III) is also reduced by Cr(II) independently of $[H^+]$ but at a much faster rate ($k_{\mathrm{Cr}} = 0.11\ M^{-1}\ s^{-1}$ at 25 °C, $\mu = 3.0$ M). An inner-sphere mechanism with attack of the reductant at the adjacent carbonyl oxygen atom has been demonstrated.[4] It is often possible to assign outer-sphere mechanisms if the ratio of rate constants $k_{\mathrm{Cr}}/k_{\mathrm{V}}$ for the reductions of a common oxidant by Cr(II) and V(II) is ca. 0.02.[11] The parallel reduction of complex II by V(II) is independent of $[H^+]$ and the ratio $k_{\mathrm{Cr}}/k_{\mathrm{V}}$ was found to be 0.021 (Table IV). This is regarded as strong evidence for the assignment of outer-sphere mechanisms for the reductions by Cr(II) and V(II). The fact that the pyridine nitrogen is in the meta position and conjugation effects are not transmitted effectively cannot account for the complete inability of pyridine-3-carboxylic acid to serve as an electron-mediating group. Vrachnou-Astra and Katakis have reported[12] that uncomplexed pyridine-2-carboxylic acid and the 4 isomer are readily reduced by Cr(II) and V(II) whereas the 3 isomer does not seem to be reduced by either of these metal ions. The nonreducibility of the free ligand is regarded to be the dominant factor determining the poor capacity of pyridine-3-carboxylic acid to mediate in electron transfer.

Specific rates for the reductions of complexes I–III by Cr(II) cover a range of four orders of magnitudes. This is contrasted by very similar rates for the reductions of these complexes by V(II) (Table IV). Values of k_{V} are small and certainly not of the substitution into $[V(H_2O)_6]^{2+}$ controlled inner-sphere type. It is concluded that V(II) reacts by an outer-sphere mechanism. This study seems to keep in line with the observation that electron transfer through extended bridging ligands is less common for V(II) than for Cr(II).[13] However, it is interesting to recall the results of Norris and Nordmeyer,[14] who reported an inner-sphere substitution-controlled mechanism for the reduction of the N-coordinated pyridine-4-carboxylatopentaamminecobalt(III) complex by V(II). Thus pyridine-4-carboxylic acid mediates an electron in this case where formation of a precursor complex via the (hard) carboxylic oxygen atom is involved, but not if complex III is reduced by V(II) (no precursor complex formation by the soft pyridine nitrogen?). We have no explanation at all as to why the nonreducible pyridine-3-carboxylic acid is capable of acting as a mediating ligand when the N-coordinated pyridine-3-carboxylatopentaamminecobalt(III) complex is reduced by V(II).[14] Complex II, on the other hand, is reduced via an outer-sphere mechanism by Cr(II) which favors an inner-sphere path whenever possible.

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Supplementary Material Available: Table I showing kinetic data for the reductions of complexes I–IV by chromium(II) (2 pages). Ordering information is given on any current masthead page.

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