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Kinetics and Mechanism of the Reduction of Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) by Chromium(II)

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The reduction of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ($\mathrm{Co^{III}}$TMpyP) by chromium(II) has been studied as a function of pH and added anions. In perchlorate medium, the observed rate constant may be written as $k_{\text{obsd}} = (k_0 + k_0'/[\mathrm{H^+}])[\mathrm{Cr^{2+}}]$, whereas in the presence of chloride ion and thiocyanate ion, catalytic pathways are introduced. For chloride $k_{\text{obsd}} = (k_0 + k_0'/[\mathrm{H^+}])[\mathrm{Cr^{2+}}] + (k_1 + k_1'/[\mathrm{H^+}])[\mathrm{Cl^-}][\mathrm{Cr^{2+}}]$, and for thiocyanate $k_{\text{obsd}} = (k_0 + k_0'/[\mathrm{H^+}])[\mathrm{Cr^{2+}}] + (k_2 + k_2'/[\mathrm{H^+}])[\mathrm{SCN^-}][\mathrm{Cr^{2+}}] + (k_3 + k_3'/[\mathrm{H^+}])[\mathrm{SCN^-}]^2[\mathrm{Cr^{2+}}]$. The relative rates for the acid-independent paths are $k_0{:}k_1{:}k_2{:}k_3 = 1{:}30{:}2 \times 10^3{:}2 \times 10^5$ while for the acid-dependent paths $k_0'{:}k_1'{:}k_2'{:}k_3' = 1{:}3{:}3 \times 10^2{:}4 \times 10^4$. A comparison of these relative rate constants with those for the chromium(II) reduction of tris(1,10-phenanthroline)cobalt(III), hexaamminecobalt(III), and tetrakis(4-pyridyl)porphineiron(III) leads to the conclusion that the acid-dependent pathways involve hydroxy-bridged transition states and that reduction of $\mathrm{Co^{III}}$TMpyP occurs through the axially bound ligands rather than through the porphyrin ring system. The reduction of the cobalt(III) porphyrin proceeds faster than the replacement of the axial water molecules by chloride or thiocyanate ions, and, therefore, in contrast to the situation for the iron(III) porphyrin which undergoes rapid ligand replacement, the added anions are not directly bonded to the cobalt(III) center in the transition state for the reduction. These studies show that the mechanism of electron transfer in these porphyrin systems is largely determined by the ease of ligand replacement at the metal center.

Introduction

The involvement of metalloporphyrin–protein complexes in oxidation–reduction reactions in living systems has generated considerable interest in the electron-transfer properties of simpler porphyrin complexes. In the hope of obtaining a deeper understanding of the mechanisms of the latter reactions we have investigated the rate of reduction of the cobalt(III) derivative of tetrakis(4-*N*-methylpyridyl)porphine ($\mathrm{Co^{III}}$TMpyP) by chromium(II) in the presence of various anions. The results are interpreted with reference to the spectral, kinetic, and thermodynamic properties of $\mathrm{Co^{III}}$TMpyP,[2] the reactivity patterns observed in other cobalt(III) reductions,[3] and the possible pathways for electron transfer.

The cobalt derivative of TMpyP is especially well suited to this type of investigation. This metalloporphyrin is water soluble over an extensive pH range and remains monomeric in solution up to at least pH 8. The Evans method[4-6] has been used to show that the metalloporphyrin is a low-spin d^6 complex. $\mathrm{Co^{III}}$TMpyP binds two water molecules in axial positions at low pH and behaves as a weak dibasic acid. The acid dissociation constants for these reactions have been determined.[2] In addition, stability constants and rate constants for the substitution reactions of $\mathrm{Co^{III}}$TMpyP with thiocyanate[2] and pyridine[7] are known. The reduction reactions of $\mathrm{Co^{III}}$TMpyP provide a useful comparison with those of $\mathrm{Fe^{III}}$TpyP since, in contrast to the water molecules occupying the axial positions of the cobalt(III) complex, the coordinated water molecules in the iron(III) complex undergo rapid replacement. The relative substitution inertness of the cobalt(III) complex permits a more detailed interpretation of the mechanistic details of its electron-transfer reactions.

Experimental Procedures

Materials. Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) was prepared according to published procedures.[8] The iron(III) derivative of tetrakis(4-pyridyl)porphine was obtained from the Mad River Chemical Co. Chromium(II) perchlorate solutions were prepared by the reduction of chromium(III) perchlorate with amalgamated zinc and were stored under argon. Sodium perchlorate solutions were made by the neutralization of sodium carbonate with perchloric acid. The resulting solutions were boiled to expel carbon dioxide, and the pH was adjusted to 4–5. Sodium chloride and sodium thiocyanate were used without further purification. All solutions were prepared with triply distilled water.

Spectral and Kinetic Measurements. Spectra were determined under anaerobic conditions on a Cary 14 spectrophotometer. The absorbance of solutions prepared by the addition of excess chromium(II) to $\mathrm{Co^{III}}$TMpyP was measured against solutions containing chromium(II) at identical concentration, ionic strength, and pH. The kinetics of the reduction of the cobalt porphyrin were followed on a Durrum Model D110 stopped-flow apparatus. For chloride ion, the kinetics were independent of the order of mixing; chloride ion added to the chromium(II) or to the cobalt porphyrin solutions gave the same results. However, experiments where thiocyanate was added to the cobalt porphyrin solution and subsequently mixed with chromium(II) solutions gave results different from those in which the thiocyanate was added to only the chromium(II) solution. In the former type of experiment several coupled effects were observed, the last of which involved a large decrease in absorbance throughout the Soret region. Multiple effects were also observed in the latter type of experiment, but the half-lives of the consecutive processes were so vastly different that kinetics of the rapid process could be investigated without appreciable difficulty. The slower effect once again led to a decreased absorbance of the solution throughout the Soret region. Kinetic measurements in which the thiocyanate was initially present in only the chromium(II) solution are reported here.

All of the reactions were run with excess reducing agent. The exponential nature of the experimental curves of absorbance *vs.* time were consistent with a first-order dependence on metalloporphyrin; good first-order behavior persisted for at least 3 reaction half-lives. The reproducibility of replicate runs was a few per cent; rate measurements using different stock solutions agreed to within 10%. We estimate the error limit in the rate constants to be ±10% except for the thiocyanate-catalyzed paths where it is closer to ±25%. All of the kinetic measurements were performed at 25.0° and an ionic strength of 0.5 *M*.

Results

Spectral Experiments. In the pH region used in this study ($3 \leqslant [\mathrm{H^+}] \leqslant 300$ m*M*), the Soret band maximum for tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) is at 434 nm.[2] Addition of chromium(II) shifts the Soret band maximum to 428

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(1) (a) Ithaca College. (b) Brookhaven National Laboratory.

(2) (a) R. F. Pasternack and M. A. Cobb, *Biochem. Biophys. Res. Commun.*, 51, 507 (1973); (b) *J. Inorg. Nucl. Chem.*, 35, 4327 (1973).

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nm with a decrease in intensity. Similar results were obtained in perchlorate and in a chloride-perchlorate mixture ($\mu = 0.5\ M$, $[H^+] = 0.2\ M$). Electrochemical reduction of tetraphenylporphinecobalt(III) also results in a shift of the Soret band to shorter wavelength.[9] Corwin, *et al.*, have suggested that the direction of this spectral shift is characteristic of metalloporphyrins bonded to axial ligands.[10] When oxygen was bubbled through the reduced metalloporphyrin solution, the Soret band shifted back to its original position although the full intensity was not restored. Evidently the reaction of the metalloporphyrin with excess chromium(II) leads to a cobalt(II) species which can be further reduced in an irreversible step.

When chromium(II) solution containing 600 μM thiocyanate is added to a $Co^{III}TMpyP$ solution ($[H^+] = 0.2\ M$), a very broad band results which can be analyzed as arising from two spectral peaks, one at about 428 nm and the other at 445 nm. The latter peak may arise from thiocyanate-complexed cobalt(II) porphyrin. While at the above thiocyanate concentration and pH the half-life for the replacement of a water molecule on $Co^{III}TMpyP$ by a thiocyanate ion would be over 15 min,[2] $Co^{II}TMpyP$ is expected to undergo substitution very rapidly.[11]

When oxygen is bubbled through the $Co^{III}TMpyP\text{-}Cr^{2+}\text{-}SCN^-$ product solution, a Soret band centered at about 435 nm develops; this band is somewhat broader than the one for the original $Co^{III}TMpyP$ solution. The Soret maximum for $Co^{III}TMpyP(H_2O)(SCN)$ is at 438 nm[2] and the spectrum observed here may be a combination of two Soret bands having maxima at 434 and 438 nm. When the thiocyanate experiment is repeated with 10 mM SCN^-, a somewhat more complicated series of reactions takes place. The initial spectrum has a maximum at 445 nm; within 2 min this maximum shifts to 430 nm (all peaks are broad); 15 min later the Soret region shows little absorbance but a Soret band (λ_{max} 443 nm) is restored when oxygen is bubbled through the solution. The peak is quite broad and could represent a mixture of the $CoP(H_2O)(SCN)$, λ_{max} 438 nm, and $CoP(SCN)_2$, λ_{max} 455 nm, absorbances.

The spectra of reduced metalloporphyrins in which the added electrons are distributed in the π system of the organic ligand have been investigated.[12] Both the one-electron and two-electron reduction products of zinc tetraphenylporphine have Soret bands at longer wavelengths and considerably decreased intensity relative to the parent compound. The ratio of the molar absorptivities of the Soret band maxima is 8:2:1 for the parent compound, the one-electron reduction product, and the two-electron reduction product, respectively. Hambright has also observed that the reduction of the porphyrin ring system leads to marked decrease of absorption band intensity although in some cases the original metalloporphyrin spectrum can be reconstituted by bubbling oxygen through the solution.[13] On the basis of these considerations we conclude that the reaction of $Co^{III}TMpyP$ with chromium(II) leads initially to a reversible reduction of the metal center and that oxygen bubbled through the solution can at least partly restore the cobalt(III) porphyrin.

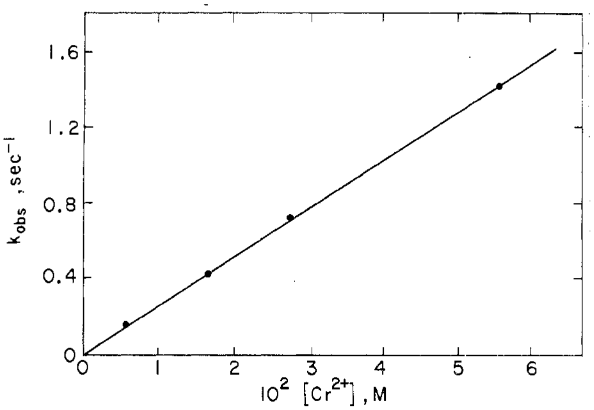

Figure 1. Plot of k_{obsd} *vs.* $[Cr^{2+}]$ in a perchlorate medium; $\mu = 0.5\ M$, temperature 25°. At a hydrogen ion concentration of 0.2 M, $k_{obsd}/[Cr^{2+}] = 25\ M^{-1}\ sec^{-1}$.

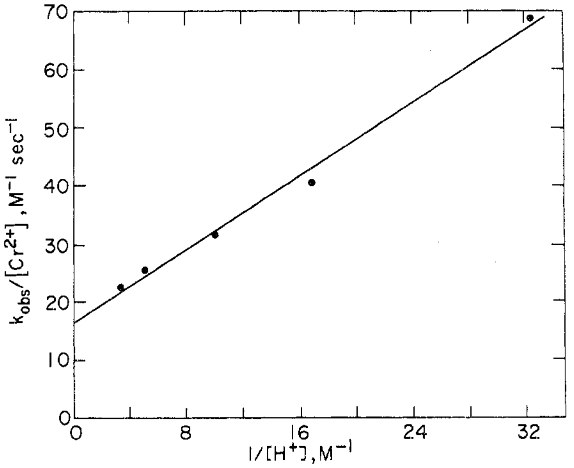

Figure 2. Acid dependence of the reduction of $Co^{III}TMpyP$ by Cr^{2+} in a perchlorate medium; $\mu = 0.5\ M$, temperature 25°. From this plot, $k_{obsd}/[Cr^{2+}] = 16 + 1.6/[H^+]$. At $[H^+] = 0.2\ M$, $(k_{obsd}/[Cr^{2+}])_{calcd} = 24\ M^{-1}\ sec^{-1}$, in good agreement with the experimentally obtained value of $25\ M^{-1}\ sec^{-1}$.

Kinetic Experiments. The kinetic data for the Cr^{2+}-$Co^{III}TMpyP$ reaction in a perchlorate medium of $[H^+] = 0.2\ M$ are shown in Figure 1. Evidently the reaction obeys good second-order kinetics. It is also apparent from Figure 2 that the observed rate constants increase with decreasing acidity; in the pH range studied the rate constants are given by

$$k_{obsd} = (k_0 + k_0'/[H^+])[Cr^{2+}] \tag{1}$$

with $k_0 = 16\ M^{-1}\ sec^{-1}$ and $k_0' = 1.6\ sec^{-1}$. The rate of reduction of $Fe^{III}TpyP$ by Cr^{2+} in perchlorate medium ($\mu = 1.0\ M$) has been reported as being acid independent.[13,14] In view of the present result for $Co^{III}TMpyP$, we decided to reinvestigate the $Fe^{III}TpyP$ system. An acid dependence of the form of eq 1 with $k_0 = 2.7 \times 10^2\ M^{-1}\ sec^{-1}$ and $k_0' = 8.0\ sec^{-1}$ was found for $Fe^{III}TpyP$ (Figure 3). The previous investigation conducted in the concentration range $10^{-3} < [H^+] < 10^{-1}\ M$ led to a value of $700\ M^{-1}\ sec^{-1}$ for $k_{obsd}/[Cr^{2+}]$. It is interesting to note that from the present result (obtained at $\mu = 0.5\ M$), $k_{obsd}/[Cr^{2+}] = 670\ M^{-1}\ sec^{-1}$ at $[H^+] = 2 \times 10^{-2}\ M$, which is about the midpoint of the range previously investigated.

The observed rate constants for the reduction of $Co^{III}TMpyP$ by chromium(II) increase with increasing chloride ion concentration (Figure 4). The chloride catalysis, too, ex-

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[10] A. H. Corwin, A. B. Chivvis, R. W. Poor, D. G. Whitten, and E. W. Baker, *J. Amer. Chem. Soc.*, **90**, 6577 (1968).

[11] The spectra were taken within 2 min of mixing the reactants.

[12] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 818 (1963).

[13] W. P. Hambright, Ph.D. Thesis, University of Chicago, Chicago, Ill., 1966.

[14] P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **4**, 912 (1965).

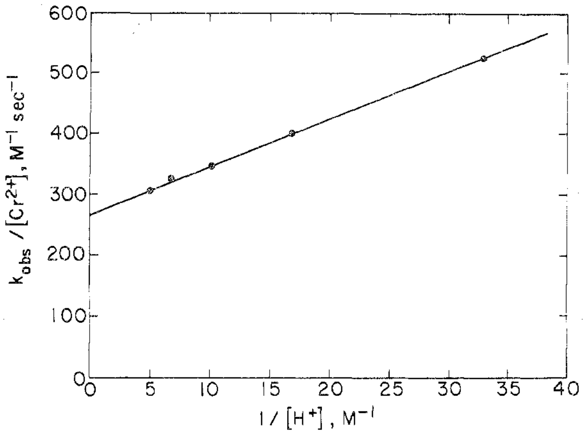

Figure 3. Acid dependence of the reduction of $Fe^{III}TpyP$ by Cr^{2+} in a perchlorate medium; $\mu = 0.5$ *M*, temperature 25°. From the plot, $k_{obsd}/[Cr^{2+}] = 270 + 8.0/[H^+]$.

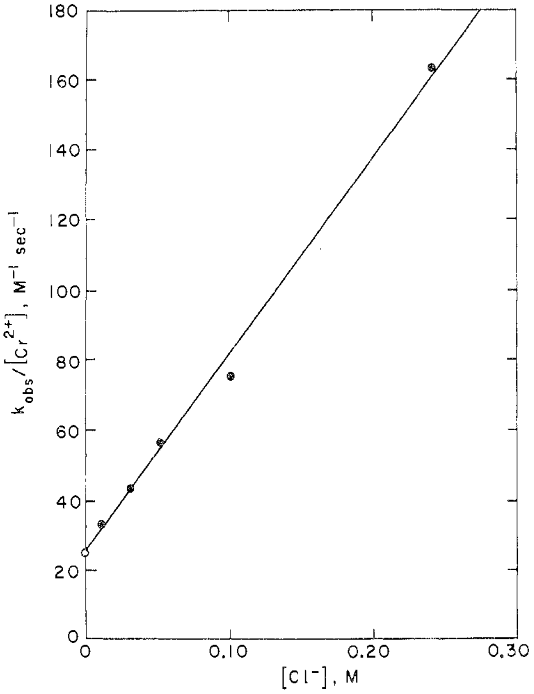

Figure 4. Chloride catalysis of the reduction of $Co^{III}TMpyP$ by Cr^{2+}; $\mu = 0.5$ *M*, temperature 25°, $[H^+] = 0.2$ *M*. The plot is described by $k_{obsd}/[Cr^{2+}] = 26 + 560[Cl^-]$. The intercept is in good agreement with the value obtained at $[H^+] = 0.2$ *M* in a perchlorate medium (open circle).

hibits an inverse acid dependence and under the conditions used the rate constants are given by

$$\frac{k_{obsd}}{[Cr^{2+}]} = k_f + \left[k_1 + \frac{k_1'}{[H^+]}\right][Cl^-] \qquad (2)$$

with $k_f = k_0 + k_0'/[H^+]$. The values of k_1 and k_1' are $4.9 \times 10^2\ M^{-2}\ sec^{-1}$ and $4.9\ M^{-1}\ sec^{-1}$, respectively (Figure 5).

The rate law, in the presence of added thiocyanate, exhibits both a dependence on $[SCN^-]$ and a dependence on $[SCN^-]^2$. The rate constant at a fixed $[H^+]$ may be written as

$$k_{obsd} = k_f[Cr^{2+}] + k_f'[Cr^{2+}][SCN^-] + k_f''[Cr^{2+}][SCN^-]^2 \quad (3)$$

Therefore, provided that the concentrations of $Cr(NCS)^+$ and $Cr(NCS)_2$ do not represent a significant fraction of the total chromium(II) concentration,[3] a plot of $(k_{obsd}/[Cr^{2+}] - k_f)/[SCN^-]$ *vs.* $[SCN^-]$ should be linear with the intercept equal to k_f' and the slope k_f''. Such a plot is shown in Figure 6; this plot gives $k_f' = 2.6 \times 10^4\ M^{-2}\ sec^{-1}$ and $k_f'' = 3.7 \times 10^6\ M^{-3}\ sec^{-1}$ at $[H^+] = 0.20\ M$. Experiments conducted as a function of $[SCN^-]$ at two values of $[H^+]$ and as a function of $[H^+]$ at two values of $[SCN^-]$ show that the best fit with the data is obtained when the observed rate constant is written as

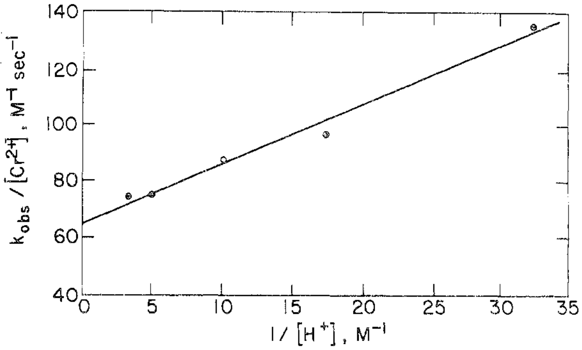

Figure 5. Acid dependence of the reduction of $Co^{III}TMpyP$ in the presence of 0.1 *M* chloride; $\mu = 0.25$ *M*, temperature 25°. The filled circles represent runs in which chloride was added to both the porphyrin solution and the chromium(II) solution. The open circle represents a datum point obtained when 0.2 *M* chloride ion was added to the chromium(II) stock solution and none was added to the porphyrin stock solution. We obtain $k_{obsd}/[Cr^{2+}] = 65.0 + 2.11/[H^+]$ in 0.1 *M* chloride. Using the chloride-independent paths determined earlier, we find $k_{obsd}/[Cr^{2+}] = (16 + 1.6/[H^+]) + (490 + 4.9/[H^+])[Cl^-]$.

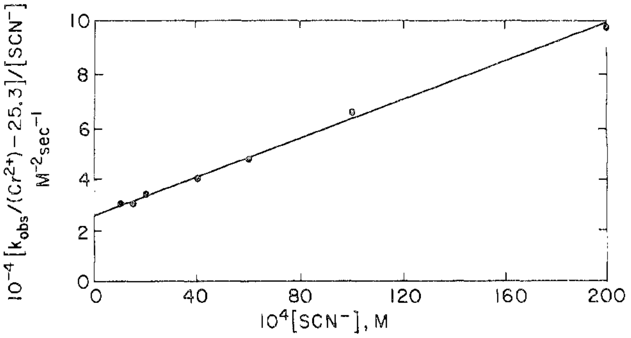

Figure 6. Thiocyanate catalysis of the reduction of $Co^{III}TMpyP$ by Cr^{2+}; $\mu = 0.5$ *M*; temperature 25°; $[H^+] = 0.2$ *M*. A plot of $[(k_{obsd}/[Cr^{2+}]) - 25.3]/[SCN^-]$ *vs.* $[SCN^-]$ has been constructed based on the assumption that neither $CrNCS^+$ nor $Cr(NCS)_2$ is present in appreciable amounts. From the linear plot, we obtain that at $[H^+] = 0.2$ *M*, the rate constant for catalysis by one thiocyanate ion is $2.6 \times 10^4\ M^{-2}\ sec^{-1}$ while for catalysis by two thiocyanate ions the rate constant is $3.7 \times 10^6\ M^{-3}\ sec^{-1}$.

$$\frac{k_{obsd}}{[Cr^{2+}]} = k_f + \left[k_2 + \frac{k_2'}{[H^+]}\right][SCN^-] + \left[k_3 + \frac{k_3'}{[H^+]}\right][SCN^-]^2 \qquad (4)$$

with $k_2 = 2.7 \times 10^4\ M^{-2}\ sec^{-1}$, $k_2' = 5.3 \times 10^2\ M^{-1}\ sec^{-1}$, $k_3 = 3.5 \times 10^6\ M^{-3}\ sec^{-1}$, and $k_3' = 6.0 \times 10^4\ M^{-2}\ sec^{-1}$.

The rate constants determined in this work are summarized in Table I.

Discussion

Perchlorate System. The dependence of the rate constant on pH in perchlorate medium shows that the reduction of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) by chromium(II) proceeds by two parallel paths, one independent of acidity and the other inversely proportional to the hydrogen ion concentration. This finding can be interpreted in terms of the reactions

$$\mathrm{CoP(H_2O)_2 + Cr^{2+}} \xrightarrow{k_0} \qquad (5a)$$

and either

$$\mathrm{CoP(H_2O)(OH) + Cr^{2+}} \xrightarrow{k_{-1}} \qquad (5b)$$

or

$$\mathrm{CoP(H_2O)_2 + CrOH^{+}} \xrightarrow{k_{-2}} \qquad (5c)$$

Since $CrOH^+$ does not appear to be an important reactant (in the pH range studied) in other systems,[15] it may be tentatively concluded that the reactants in the inverse acid path are $CoP(H_2O)(OH)$ and Cr^{2+} and, consequently, that $k_0' = K_{a1}k_{-1}$ where K_{a1} is the first acid dissociation constant of Co^{III}TMpyP. The value of pK_{a1} is 5.9[2] and thus $k_{-1} = 1.3 \times 10^6\ M^{-1}\ sec^{-1}$.[16]

The relatively high value of k_{-1}/k_0 implies that hydroxide is bonded to both cobalt(III) and chromium(II) in the transition state for the acid-dependent reaction.[17,18] This transition state may be represented as $[Co\text{-}OH\text{-}Cr]^{\ddagger}$. Transition states of this type have been widely proposed for reactions between transition metal complexes featuring large inverse acid dependences.[15] This interpretation does not require that the transition state for the acid-independent pathway be water bridged; indeed a transition state in which the two metal centers are separated by two water molecules (outer-sphere mechanism) is also consistent with the kinetic data and may well afford the preferred pathway for the acid-independent reaction.[19]

Chloride and Thiocyanate Effects. Fairly definite conclusions can be drawn concerning the mechanism of the reduction of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) by chromium(II) in the presence of chloride and thiocyanate ions. Since the catalyzed reduction proceeds faster than the rate of water replacement on the cobalt(III) center, the catalyzed reactions cannot proceed *via* transition states in which the added anion is bonded to the cobalt(III). The rate law for the acid-independent pathway establishes that the transition state for this reaction contains $CoP(H_2O)_2$, X^-, and Cr^{2+}. Since X^- is not bonded to the cobalt(III) center prior to the reduction, the transition state for the acid-independent reaction is formed either from the pair of reactants $CoP(H_2O)_2,X^-$ and Cr^{2+} or from $CoP(H_2O)_2$ and CrX^+, where $CoP(H_2O)_2,X^-$ represents an ion pair formed between the cobalt porphyrin and X^- and CrX^+ denotes a complex of Cr^{2+} and X^-. The kinetic data do not distinguish between these alternatives. Additional information about the reaction mechanism can, however, be obtained if it is assumed that the electron conductivities of H_2O and NH_3 are similar and that the electron-transfer properties of the porphyrin ring system are similar to those of phenanthroline. With the aid of these assumptions it becomes possible to compare the reactivity pattern found in this work with the pattern previously determined for the reduction of $Co(NH_3)_6^{3+}$ and $Co(phen)_3^{3+}$ by chromium(II).[3]

The relative values of the rate constants for the acid-independent paths in the perchlorate, chloride, and thiocyanate systems ($k_1/k_0 = 30$, $k_2/k_1 = 55$) are more similar to the reactivity ratio seen in the chromium(II) reduction of $Co(NH_3)_6^{3+}$ ($k_1/k_0 = 11$, $k_2/k_1 = 61$) than of $Co(phen)_3^{3+}$ ($k_1/k_0 = 6$, $k_2/k_1 = 1.3 \times 10^3$).[3] This is consistent with the assignment of an outer-sphere mechanism to the anion-catalyzed, acid-independent reduction of $CoP(H_2O)_2$ (for there is no doubt but that an outer-sphere mechanism operates in the reduction of $Co(NH_3)_6^{3+}$) and suggests further that the electron transfer to the cobalt(III) does not take place through the porphyrin ring system (since the reactivity pattern differs from that found for $Co(phen)_3^{3+}$). The transition state for the anion-catalyzed, acid-independent reaction may thus be represented as $[Co\text{-}H_2O\text{-}X\text{-}Cr]^{\ddagger}$. Electrostatic considerations render it likely that the anion is located between the two metal centers.

Table I. Rate Constants for the Reduction of Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) and Tetrakis(4-*N*-pyridyl)iron(III) by Chromium(II)[a]

Term	Rate constant
$k[CoP(H_2O)_2][Cr^{2+}]$	$16\ M^{-1}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}]/[H^+]$	$1.6\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][Cl^-]$	$4.9 \times 10^2\ M^{-2}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][Cl^-]/[H^+]$	$4.9\ M^{-1}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][SCN^-]$	$2.7 \times 10^4\ M^{-2}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][SCN^-]/[H^+]$	$5.3 \times 10^2\ M^{-1}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][SCN^-]^2$	$3.5 \times 10^6\ M^{-3}\ sec^{-1}$
$k[CoP(H_2O)_2][Cr^{2+}][SCN^-]^2/[H^+]$	$6.0 \times 10^4\ M^{-2}\ sec^{-1}$
$k[FeP(H_2O)_2][Cr^{2+}]$	$2.7 \times 10^2\ M^{-1}\ sec^{-1}$
$k[FeP(H_2O)_2][Cr^{2+}]/[H^+]$	$8.0\ sec^{-1}$
$k[FeP(H_2O)_2][Cr^{2+}][Cl^-]$	$9.1 \times 10^5\ M^{-2}\ sec^{-1}$ [b]
$k[FeP(H_2O)_2][Cr^{2+}][SCN^-]$	$2.3 \times 10^7\ M^{-2}\ sec^{-1}$ [b]

[a] The error limit in the rate constants is estimated to be ±10% except for the thiocyanate-catalyzed paths where it is closer to ±25%. Except for the last two entries in the table all of the measurements were performed at 25° and an ionic strength of 0.5 *M* maintained with sodium perchlorate. The last two reactions were studied at an ionic strength of 1.0 *M*. [b] References 13, 14.

A very different situation exists in the chromium(II) reduction of tetrakis(pyridyl)porphineiron(III).[14] Here the $k_0{:}k_1{:}k_2$ ratio is $1{:}1.2 \times 10^3{:}3.3 \times 10^5$.[20] The iron(III) system differs from the cobalt(III) system in at least one important respect: the water molecules coordinated to the metal center in the iron(III) porphyrin are substitution labile, while those in the cobalt(III) system are inert to substitution, at least on the time scale of the electron-transfer reactions. Consequently, while an anion-bridged transition state could be ruled out for the cobalt(III) reduction, such a transition state could obtain in the reduction of the iron(III) porphyrin. In fact there is good evidence that the chloride- and thiocyanate-catalyzed reductions of tetrakis(pyridyl)porphineiron(III) do indeed proceed *via* anion-bridged transition states. Thus the effect of chloride on the reduction rate is relatively large (however, see the discussion of the vanadium(II) result below) and, perhaps more convincing, $CrSCN^{2+}$ has been identified as a product of the thiocyanate-catalyzed reduction of the iron(III) porphyrin in perchlorate media.[21]

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(15) A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

(16) Although the pK_a of chromous ion has not been determined, we assume that it is larger than 6. Substitution of this pK_a limit leads to an even larger value of k_{-1} than has been estimated above.

(17) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(18) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968).

(19) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

(20) In common with the authors of ref 14, we will assume that the acid dependence of the anion effects in the iron(III) system is small. If our interpretation of the mechanisms of the reduction of the metal porphyrins by chromium(II) is correct, then for the inner-sphere reduction of Fe^{III}TpyP in the presence of chloride or thiocyanate, an inverse hydrogen ion dependent pathway can arise only from the loss of a proton from the remaining water molecule on the iron porphyrin or from the involvement of $CrOH^+$; neither of these effects is likely to be large. In this connection it should be noted that replacement of a coordinated water molecule in Co^{III}TMpyP by an anion shifts the pK_a of the remaining water molecule by as much as 5 units.[2]

(21) T. J. Przystas, A. P. Forman, and N. Sutin, unpublished observations.

In this connection it is of interest that the reduction of tetraphenylporphineiron(III) chloride by chromium(II) in benzene solution produces CrCl^{2+}. Evidently this reaction, too, proceeds *via* an anion-bridged transition state.[22]

The effect of added anions on the rate of reduction of Fe^{III}TpyP by vanadium(II) has also been studied.[13,14] In these experiments the anions were added to the porphyrin solutions only. Since the measured reduction rates were greater than the rate of water loss from the hexaaquovanadium(II) ion,[17] the added anions cannot be bridging the two metal centers in the transition state. This situation is thus similar to the one for Co^{III}TMpyP. Yet the catalytic effects observed for the reduction of Fe^{III}TpyP by vanadium(II) are comparable to those observed for the reduction of Fe^{III}TpyP by chromium(II) and much larger than those observed for the reduction of Co^{III}TMpyP by chromium(II). This observation further demonstrates that it is necessary that the anion be bonded to the metal center of the porphyrin for large anion effects to be observed.

Finally, the rate of the inverse acid path is also enhanced by added chloride and thiocyanate ions. An ambiguity concerning the nature of the reactants again arises: the reactants could either be the ion pair CoP(H$_2$O)(OH),X$^-$ and Cr^{2+} or be CoP(H$_2$O)(OH) and the chromium(II) complex CrX$^+$, for the reaction of either pair of reactants could yield the hydroxide-bridged transition state. The relatively small effect of chloride on the inverse acid path ($k_1'/k_0' = 3$) shows that the hydroxide-bridged transition state benefits less from the presence of a chloride ion than does the transition state in the acid-independent reaction ($k_1/k_0 = 30$); by contrast, the hydroxide-bridged transition state derives relatively more benefit from the presence of a thiocyanate ion ($k_2'/k_1' = 1 \times 10^2$, $k_2/k_1 = 6 \times 10$). This comparison provides mild evidence for the operation of a hydroxide and thiocyanate doubly bridged mechanism. In such a mechanism, hydroxide might bridge the two metal centers while thiocyanate coupled the chromium to the porphyrin ring system. This effect could be synergistic in the sense that the hydroxide coordinated to the cobalt could withdraw electrons from the porphyrin ring system thereby making it more positive and a better site for attachment of the nucleophilic sulfur atom of thiocyanate. Addition of a second thiocyanate ion to the transition state appears to benefit the acid-independent and the inverse acid paths about equally.

In conclusion, these studies show that different mechanisms operate in the chromium(II) reductions of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) and tetrakis(pyridyl)-porphineiron(III). The reduction of the iron(III) complex is much more sensitive to the effect of added anions than is the reduction of the cobalt(III) complex, a result which we have rationalized in terms of the ease of substitution at the two metal centers. Coordination to the metal center of the porphyrin system seems to be required for the operation of large anion effects; conversely, when the axial sites on the metal center are blocked (by nonbridging ligands), the effect of added anions is relatively small. This conclusion is consistent with the effect of anions on the rate of reduction of ferricytochrome *c* by chromium(II); the anion effects observed in this system are smaller when both iron–protein bonds are intact than when one of the iron–protein bonds is intact and the other broken.[23]

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Mass Spectrometry of Square-Planar Rhodium(I)-β-Diketonate Complexes

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A number of square-planar monovalent rhodium–β-diketonate coordination compounds have been investigated by both low-resolution and high-resolution mass spectrometry. Fragmentation patterns were studied on the basis of the exact isotopic masses and intensities obtained by use of the computerized TPEAKS program. The composition of ions could thus be accurately determined and new insights of the fragmentation patterns of previously investigated compounds were obtained. Attention has also been focused on the mass spectroscopy of complexes with two bulky bidentate ligands. The mass spectra are simple and the presence of the metal atom plays an important role in the fragmentation paths of the ligands observed. The general course of fragmentation is rationalized in terms of the stability of the ions formed and follows established trends in rhodium organic chemistry. Intramolecular rearrangements involving the metal atom have been proposed. Diastereoisomeric rhodium complexes have also been investigated and for the first time chemical ionization mass spectra of square-planar d^8 transition metal complexes have been obtained.

Introduction

Mass spectrometry of metal complexes has received increased attention in recent years.[2-4] Most of the work reported is concerned with investigations of complexes containing monodentate ligands such as CO, olefins, or group V

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