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# Kinetic and Thermodynamic Properties of Chromium(III) Complexes Containing Pyrazine Radical Ligands

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Green complexes of 1:1 stoichiometry are formed when solutions of chromous ion and pyrazine are mixed; complexation is accompanied by proton binding at the remote nitrogen site on the ring. The association constant for monoprotonated pyrazine binding is $K_1 = 1.5 \times 10^4$ M^{-1} at 20.6 °C, $\mu = 0.10$ M. The association–dissociation kinetics were studied by using combined stopped-flow relaxation techniques; a single relaxation curve was obtained for which $\tau^{-1} = k_f[\text{Cr(II)}][\text{pyrazine}] + k_r$; the upper limit for coordination by monoprotonated pyrazine, $k_1 \leq 3.6 \times 10^6$ M^{-1} s^{-1} at 28 °C, $\mu = 0.10$ M, was about 10^2-fold slower than anticipated for rate-limiting substitution on chromous ion. In the presence of excess pyrazine the green complex disappears in a biphasic manner; the fast bleaching reaction gave rise to a 69-line EPR signal, identified as the dihydropyrazine radical cation. The reaction was described by the equilibrium (where pyz = pyrazine)

$$\text{Cr(pyzH)}^{3+} + \text{pyzH}^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{pyzH}_2^+ + \text{Cr}^{\text{III}}(\text{pyz})^{3+}$$
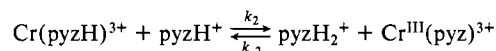
for which $K_2 = 1.3$, $k_2 \simeq 14$ M^{-1} s^{-1}, and $k_{-2} \simeq 10$ M^{-1} s^{-1} at 20.6 °C, $\mu = 0.10$ M. A transitory species with spectral features nearly identical with the Cr(pyzH)$^{3+}$ ion was formed when solutions containing chromous and pentaammine-(pyrazine)cobalt(III) ions were mixed; the colored species decayed rapidly ($t_{1/2} \simeq 100$ ms). Application of temperature-jump perturbation immediately after mixing yielded a single relaxation curve which could not be fitted to a simple mechanism. Evidence favoring formulation of the green species as chromium(III)-bound ligand radicals is discussed.

Introduction

Research in this laboratory during the last few years has been directed toward characterizing elementary steps in electron transfer.[2–3] Most recently, we have begun investigating reactions between coordination compounds for which net electron transfer is thought to proceed in stepwise fashion with intermediate formation of ligand radical anions, i.e., the chemical mechanism.[4]

Considerable evidence has accumulated to suggest the radicals of this nature form during chromous ion reduction of pentaamminecobalt(III) ions containing pyrazine (pyz) and related nitrogen heterocyclic ligands.[5–8] Although such reactions would appear to offer a unique opportunity to study simple electron transfer between ligand-based orbitals and metal centers, their redox mechanisms have not been unequivocally established. The dynamic properties of chromous ion reduction of pentaammine(pyrazine)cobalt(III) ion (A$_5$Co(pyz)) and the solution behavior of Cr(pyzH)$^{3+}$ ion described in this paper are more complex than might have been anticipated on the basis of previous mechanistic discussions of similar systems.[6,8]

Experimental Section

Materials. Synthesis of (Pyrazine)pentaamminecobalt(III) Trifluoromethanesulfonate. Trifluoromethanesulfonic acid (3M Flurochem Acid FC-24) was purified by diluting 1:1 (v/v) with water at 0 °C followed by adding solid barium hydroxide to precipitate inorganic sulfate. Excess barium ion was removed by ion-exchange chromatography on Dowex 50W-X8 resin in the H$^+$ form. Eluate trifluromethanesulfonic acid solutions were standardized by titrating with tris(hydroxymethyl)aminomethane and were converted as needed to the anionic form by adding solid sodium carbonate.

Aquopentaamminecobalt(III) trifluoromethanesulfonate was prepared by adding a stoichiometric equivalent of CF$_3$SO$_3$H solution to carbonatopentaamminecobalt(III) nitrate[9] and heating at 80 °C until all solids dissolved. Slow cooling yielded a crystalline product which was filtered, washed successively with water, ethanol, and diethyl ether, and vacuum dried.

(Pyrazine)pentaamminecobalt(III) ion was prepared by dissolving the A$_5$Co(aquo) complex in 1-methyl-2-pyrrolidinone containing approximately 10-fold excess pyrazine and immersing the solution in an oil bath preheated to 90 °C. The solution was kept over 3A molecular sieve and vented through a Drierite-filled drying tube to exclude moisture and was stirred magnetically. The reaction was judged complete when the color had changed from rose to red-orange (about 30 min). Upon cooling of the mixture, the solvent was removed by vacuum distillation (32 °C at 0.3 torr) and the complex precipitated from the dark orange residue by adding diethyl ether. Recrystallization from ethanol–diethyl ether and aqueous 5 M sodium trifluoromethanesulfonate gave a pale orange solid which was washed with ethanol and diethyl ether and vacuum dried. Spectrophotometric analysis gave λ_{max} (log ϵ_λ) 473 (1.79), 267 (3.69), and 235 (3.89). Spectral parameters were identical with those of another preparation which gave the following elemental analyses. Calcd for [(NH$_3$)$_5$Co(C$_4$H$_4$N$_2$)](CF$_3$SO$_3$)$_3$: C, 12.52; H, 2.86; N, 14.62; F, 25.43. Found: C, 12.19; H, 2.90; N, 14.34; F, 22.1. Analyses were made at the Stanford Microanalytical Laboratory.

Reagent solutions of the A$_5$Co(pyz) complex were prepared immediately before use; concentrations were determined by weight.

Other Materials. Chromous ion was prepared by reducing oxygen-purged solutions of hexaaquochromic ion with zinc amalgam. Chromic perchlorate stock solutions were prepared by reducing primary standard potassium dichromate with hydrogen peroxide; concentrations were established by spectrophotometric analysis for chromate ion.[10] Pyrazine solutions were generally prepared immediately before use, although no evidence of deterioration was found in solutions aged as long as 1 month; pyrazine purified by sublimation also gave identical results. Solution concentrations were determined spectrophotometrically by using λ_{max} (log ϵ_λ) = 260 (3.765). Aqueous solutions of dihydropyrazine radical cation used for EPR analysis were made by irradiating 2.5×10^{-2} M pyrazine in 1 M HClO$_4$, 5% 2-propanol for a few minutes with ultraviolet light from a 200-W mercury–xenon compact arc source. Lithium perchlorate stock solutions were prepared by titrating lithium carbonate with perchloric acid. Other chemicals

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(2) Norton, K. A., Jr.; Hurst, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 7237. Hurst, J. K. *Ibid*, **1976**, *98*, 4001.
(3) Farr, J. K.; Hulett, L. G.; Lane, R. H.; Hurst, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 2654. Hurst, J. K.; Lane, R. H. *Ibid.* **1973**, *95*, 1703.
(4) Halpern, J.; Orgel, L. E. *Discuss. Faraday Soc.* **1960**, *29*, 7.
(5) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4731.
(6) Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 4360.
(7) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6674.
(8) Spiecker, H.; Wieghardt, K. *Inorg. Chem.* **1977**, *16*, 1290.

(9) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 171.
(10) Baltisberger, R. J.; King, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 795.
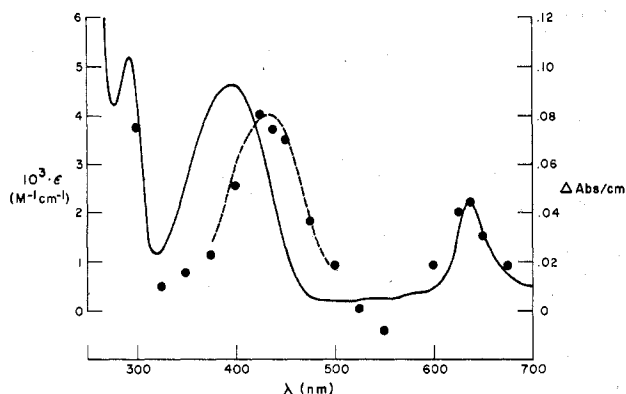
Figure 1. Electronic absorption spectra of chromium–pyrazine ions: solid line, $Cr(pyzH)^{3+}$ ion; data points, initial amplitudinal displacement when equal volumes of 1.0 mM solutions of $A_5Co(pyz)$ and Cr(II) ions are mixed at $[H^+] = 0.01$ M, $\mu = 0.10$ M, and 0 °C.

were reagent grade and used without further purification. Water was purified by using a Culligan ion-exchange reverse-osmosis system.
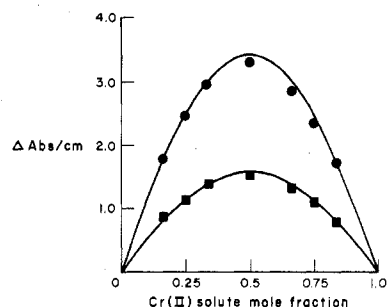
All experiments were done under argon or nitrogen; traces of oxygen were removed from these gases by passing them through two scrubbing towers filled with ~0.3 M acidified chromous ion over zinc amalgam. All measurements were made in 0.1 M ionic strength; lithium perchlorate was added when necessary to maintain constant ionic strength.

Methods. Optical measurements were routinely made on a Cary Model 16 spectrophotometer equipped with scan drive and recorder. Temperature control was provided by a thermostated water bath and circulator; temperatures were read at the cuvette surface by using a copper–constantan thermocouple. The instrument was also equipped with a syringe-drive assembly which allowed moderately rapid mixing and filling of 0.3-mL optical cuvettes (dead time $\simeq$ 1.0 s); this apparatus was used to study the extent of formation of the colored $Cr(pyzH)^{3+}$ ion under conditions where its bleaching reactions were rapid and, in conjunction with a Tektronix optical multichannel analyzer, to obtain its absorption spectrum. Otherwise, pyrazine–chromous ion binding equilibria and the kinetics of the bleaching reactions were measured by direct syringe injection of chromous ion into anaerobic solutions of the ligand in septum-stoppered optical cells. Initial absorbancies were obtained in these instances by back-extrapolation of kinetic decay traces to time of mixing (about 20 s); decay half-times varied from 2 min to several hours over the experimental range of investigation.

Kinetics of pyrazine–chromous ion association and chromous ion oxidation by $A_5Co(pyz)$ ion were studied by using combined stopped-flow temperature-jump relaxation methods, in which temperature perturbation is applied immediately after mixing reactants. The apparatus used is patterned after designs of Hammes and co-workers[11,12] and has been fitted with reservoir cells which allow in situ purging of oxygen and direct loading of drive syringes. The magnitude of the temperature "pulse" was varied by changing voltages on the discharge capacitor; calibration of voltage against temperature rise was made by using a phenol red solution at pH 8.13.[13] Reactions were monitored by measuring intensities of monochromatic light passing through the cell; in general, 640-nm wavelength light was used, which corresponds to the visible absorption maxima for both the $Cr(pyzH)^{3+}$ ion and the transients in the $A_5Co(pyz)$ vs. Cr^{2+} ion redox reaction (Figure 1), although other wavelengths where absorption occurred gave equivalent results. Traces were recorded on a Tektronix 549 storage oscilloscope and photographed for subsequent analysis.[11]

The apparatus was also used in its stopped-flow mode to obtain the absorption spectrum of redox transients in the cobalt–chromium redox reaction, which was determined by measuring the initial photomultiplier voltage displacement following mixing. Product solutions are essentially colorless at most wavelengths, so that the final voltage reading corresponds nearly to 100% transmittance.

Electron paramagnetic resonance spectra were recorded by using a Varian E-3 X-band spectrometer equipped with a variable-temperature probe. Solid spectra were taken in 50% glycerol glasses at

(11) Lane, R. H.; Hurst, J. K. *Biochemistry* **1974**, *13*, 3292.
(12) French, T. C.; Hammes, G. G. *Methods Enzymol.* **1969**, *16*, 3.
(13) Banyasz, J. L.; Stuehr, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 7226.

Figure 2. Job diagram of Cr(II)–pyz association at $[Cr]_T + [pyz]_T = 4.0$ mM, $[H^+] = 0.01$ M, $\mu = 0.10$ M, and 20.6 °C: circles, $\lambda = 400$ nm; squares, $\lambda = 636$ nm. Data points are averages of duplicate determinations. Solid line is the theoretical curve for 1:1 binding with $K_1' = 5.0 \times 10^2$ M^{-1}, $\epsilon_{400}(Cr(pyzH)^{3+}) = 4.5 \times 10^3$ M^{-1} cm^{-1}, and $\epsilon_{636}(Cr(pyzH)^{3+}) = 2.1 \times 10^3$ M^{-1} cm^{-1}.

−150 °C; solution spectra were taken by using a flat quartz cell. Reagent solutions were prepared and loaded directly into septasealed oxygen-purged tubes by using syringe techniques. Instrument accuracy was checked by calibration with 2,2-diphenyl-1-picrylhydrazide; the standard gave a g value of 2.004$_6$, which is in reasonable agreement with the accepted value of $g = 2.0037$.[14]

Results

General Observations. Intensely absorbing bright green species are formed when oxygen-free solutions of chromous ion and pyrazine are mixed; the extent of color formation, which is instantaneous, is dependent upon reagent concentrations and the solution acidity. The color slowly fades in a biphasic manner, with both the rate and magnitude of the fast phase being dependent upon concentrations of pyrazine and acid. A similar green transitory species forms when chromous ion is mixed with solutions of the $A_5Co(pyz)$ ion, but here bleaching is so rapid that color formation can be detected only with flow instrumentation. The extent of coloration in this instance is pH independent.

Chromium(II)–Pyrazine Equilibria. The electronic absorption spectrum of the green complex is given in Figure 1. Spectral band shapes are invariant with $[H^+]$ (pH 1.0–2.0), with temperature (0–40 °C), and with chromium–pyrazine ratios ($[Cr(II)]/[pyz] = 0.2$–5.0); relative maxima of the three absorption bands are constant over this range of solution conditions. Analysis by the method of varying mole ratios indicates 1:1 metal/ligand stoichiometry for the absorbing species at pH 1–2; representative data are given in Figure 2. Molar absorptivities were calculated from the relation[15]

$$[Cr]_T[pyz]_T/(\Delta A/cm) = \{[Cr]_T + [pyz]_T + (K_1')^{-1}\}/\Delta\epsilon \tag{1}$$

for which $[Cr]_T$ and $[pyz]_T$ are the total concentration of added reactants, $\Delta A/cm$ ($= A/cm - (\epsilon_{Cr}[Cr]_T + \epsilon_{pyz}[pyz]_T)$) is the deviation in absorbance from Beer's law measured immediately after mixing, $\Delta\epsilon$ ($= \epsilon_{complex} - \epsilon_{Cr} - \epsilon_{pyz}$) is the difference in molar absorptivities for complex and reactants, respectively, and K_1' ($= [complex]/[Cr][pyz']$) is the complex association constant. The prime is taken to indicate that the association constant is apparent since at the acidities investigated, pyrazine exists substantially in both its free base and monoprotonated forms, i.e., $[pyz'] = [pyz] + [pyzH^+]$. Equation 1 is valid when $[complex]^2 \ll [Cr]_T[pyz]_T$; this condition is adequately met by holding $[Cr]_T$ (5–25 mM) in large excess over $[pyz]_T$ (0.2–0.5 mM). Plots of the left side vs. $[Cr]_T + [pyz]_T$ gave good straight lines; $\Delta\epsilon$ values were determined from the re-
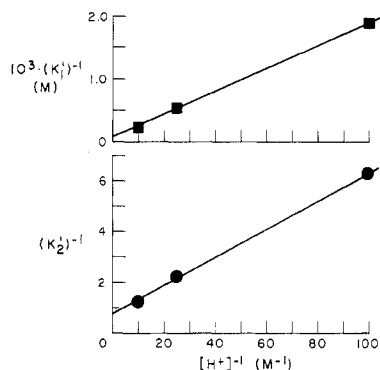
(14) See, e.g., Drago, R. S. "Physical Methods in Chemistry"; Saunders: Philadelphia, 1977.
(15) Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw-Hill: New York, 1961; pp 276–7.

Figure 3. Acid dependence of equilibrium constants at 20.6 °C and $\mu = 0.10$ M.

ciprocals of the slopes by linear regression analysis to be $\Delta\epsilon_{636} = 2.2_3 \times 10^3$ M^{-1} cm^{-1} and $\Delta\epsilon_{400} = 4.6_4 \times 10^3$ M^{-1} cm^{-1}. Since the reactants are essentially nonabsorbing in the visible region, $\Delta\epsilon \simeq \epsilon_{complex}$. The absorptivities were independent of acid over the range, pH 1.0–2.0.

The association constant, $K_1{}'$, could in principle also be determined from the slope/intercept ratio of the plots. At the highest acidities studied, however, binding was so strong that the intercept fell too close to the plot origin to obtain an accurate number; $K_1{}'$ was therefore determined from measured absorbancies of more dilute solutions by using known $\epsilon_{complex}$ values to determine complex concentrations. Values obtained for $K_1{}'$ in 0.1 M ionic strength solutions at 20.6 °C are as follows: at [H$^+$] = 0.1 M, 4.4×10^3 M^{-1}; at [H$^+$] = 0.04 M, 1.8×10^3 M^{-1}; at [H$^+$] = 0.01 M, 5.3×10^2 M^{-1}. These numbers are averages of 4–16 individual determinations whose range of values was approximately ±5%. The pH dependence of $K_1{}'$ was fitted to the equation
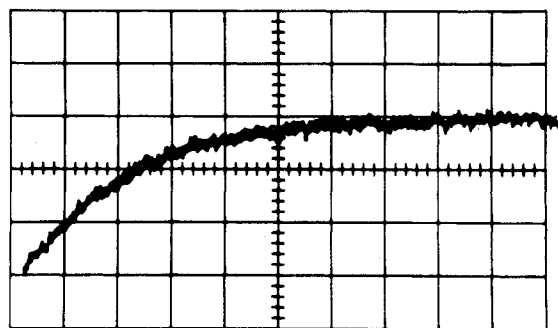
$$K_1{}' = a/(1 + b/[\text{H}^+]) \qquad (2)$$

When plotted in double reciprocal form (Figure 3), the parameters obtained were $a = 1.5 \times 10^4$ M^{-1} and $b = 0.27$ M. On identification of b with the acid dissociation constant for pyzH$^+$,[16] i.e., $b = K_a = [\text{pyz}][\text{H}^+]/[\text{pyzH}^+]$, it follows that $a = K_1 = [\text{Cr}(\text{pyzH})^{3+}]/[\text{Cr}^{2+}][\text{pyzH}^+]$. Formation of the green complex therefore requires coordination of both chromous ion and a proton to the pyrazine ligand.

The dependence of the fast bleaching reaction upon concentration of free pyrazine suggests a reversible redox equilibrium of the form

$$\text{Cr}(\text{pyzH})^{3+} + \text{pyz} + \text{H}^+ \rightleftarrows \text{Cr}(\text{pyz})^{3+} + \text{pyzH}_2{}^+ \qquad (3)$$
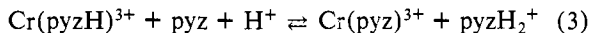
The dihydropyrazine radical cation, pyzH$_2{}^+$, has been demonstrated to be the predominant form of reduced pyrazine radical in acidic media.[18] In this instance, its formation was confirmed by EPR spectroscopy. Analysis of room-temperature solutions containing chromous ion and excess pyrazine gave well-resolved 69-line spectra centered at $g = 2.008$ which were identical with both the published spectrum[18] and the spectrum of photolytically generated pyzH$_2{}^+$ ion taken on our instrument. In the presence of a large excess of Cr^{2+} ion, where the fast bleaching reaction was not observed and equilibrium calculations (vide infra) indicated that pyzH$_2{}^+$ comprised less than 5% of the total radical ion present, no EPR signal attributable to Cr(pyzH)$^{3+}$ ion could be detected. Examination
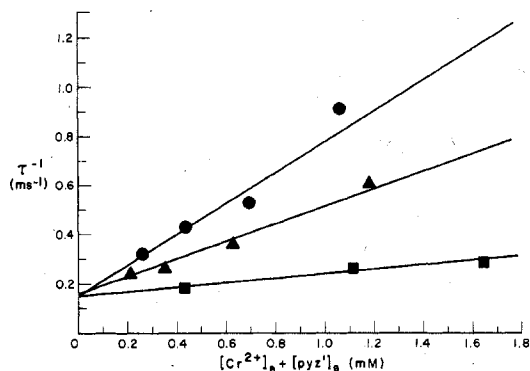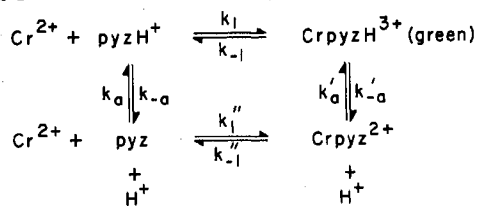
(16) Literature values range from $K_a = 0.08$ to 0.25 M, with most recent determinations giving the higher numbers.[17]
(17) Chia, A. S.; Trimble, R. F., Jr. *J. Phys. Chem.* **1961**, *65*, 863.
(18) Bolton, J. R.; Carrington, A.; Santos-Veiga, J. *Mol. Phys.* **1962**, *5*, 465. Zeldes, H.; Livingston, R. *J. Phys. Chem.* **1972**, *76*, 3348 and references therein.

Figure 4. Oscilloscope trace of relaxation observed in a Cr(II)–pyz solution at [Cr]$_T$ = [pyz]$_T$ = 3.0 mM, [H$^+$] = 0.10 M, and 8 °C: amplitude = 5 mV/cm; sweep time = 500 μs/cm; λ = 640 nm; perturbation applied $\sim$100 ms after mixing.

of the radical ions in 50% glycerol glasses at -150 °C also gave no evidence of a signal from Cr(pyzH)$^{3+}$ ion, although a broad (width = 80 G) signal centered at $g = 2.008$ was obtained with pyzH$_2{}^+$. The latter peak disappeared over a period of several days when solutions were held at room temperature, giving rise to an even broader signal at $g = 1.978$ which appeared identical with that of hexaaquochromic ion. Total concentrations of radical ion species in these solutions ranged from 0.1 to 0.5 mM.

The pyzH$_2{}^+$ radical cation was also identified spectrophotometrically; the ion possesses a strong ultraviolet band at about 315 nm.[19] When chromous ion is mixed with excess pyrazine, the initially formed UV maximum at 294 nm shifts to about 310 nm at the same rate that the visible absorption bands disappear, consistent with Cr(pyzH)$^{3+} \rightarrow$ pyzH$_2{}^+$ conversion. Oxygenation of the reaction solution at this point removes all radical ions; the difference (reduced – oxidized) gives the spectrum of radical ions present, which was found to be identical with that published for the pyzH$_2{}^+$ ion.[19]

Quantitative assessment of the redox equilibria given by (3) was made in the following way. In runs where the fast and slow components of the Cr(pyzH)$^{3+}$ ion decay curves were well separated, it was possible to estimate the total loss of Cr(pyzH)$^{3+}$ ion in the redox equilibration process by back-extrapolation of the slow component to the time of mixing. Although this procedure tacitly assumes that the slow decay is zero order, this process is sufficiently slow ($t_{1/2} \approx$ hours) that kinetic curves from this reaction are essentially linear over the time course of the fast equilibration process ($t_{1/2} \approx$ minutes). The equilibrium concentration of Cr(pyzH)$^{3+}$ ion could therefore be calculated from the corrected absorbance and its known ϵ value. Making use of stoichiometric relationships and previously determined $K_1{}'$ values, it was then possible to calculate the concentration of all species given in (3), hence, an apparent equilibrium constant. Defining $K_2{}' = [\text{pyzH}_2{}^+][\text{Cr}(\text{pyz})^{3+}]/[\text{Cr}(\text{pyzH})^{3+}][\text{pyz}']$, we found at 20.6 °C, $\mu = 0.1$ M, $K_2{}'$ as follows: at [H$^+$] = 0.10 M, 0.81; at [H$^+$] = 0.04 M, 0.45; at [H$^+$] = 0.01 M, 0.16. These numbers are averages of 4–24 individual determinations whose range of values was approximately ±20%. The acid dependence of $K_2{}'$ fits the functional form given by (2); here, if $b = K_a$, $a = K_2 = [\text{pyzH}_2{}^+][\text{Cr}(\text{pyz})^{3+}]/[\text{Cr}(\text{pyzH})^{3+}][\text{pyzH}^+]$. From the plot in double reciprocal form (Figure 3), we obtain $K_a \simeq 0.07$ M, $K_2 = 1.3$. The value of K_a is in only fair agreement with that determined from the association equilibrium but, in view of the relatively large errors in these measurements, seems acceptable.

Kinetics of Cr(pyzH)$^{3+}$ Ion Formation and Redox Equilibration. A relaxational response was seen when tempera-

(19) Moorthy, P. N.; Hayon, E. *J. Phys. Chem.* **1974**, *78*, 2615.

Scheme I

$$Cr^{2+} + pyzH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CrpyzH^{3+} (green)$$

$$Cr^{2+} + pyz \underset{k_{-1}''}{\overset{k_1''}{\rightleftharpoons}} Crpyz^{2+}$$

$$+ \qquad\qquad +$$
$$H^+ \qquad\qquad H^+$$

Figure 5. Concentration dependence of the Cr(II)-pyz relaxation at 20.5 °C, μ = 0.10 M: circles, [H$^+$] = 0.10 M; triangles, [H$^+$] = 0.030 M; squares, [H$^+$] = 0.010 M. Data points are averages of at least six individual measurements. The solid lines are weighted least-squares fits to the data according to eq 4.

ture-jump perturbation was applied immediately after mixing chromous ion and pyrazine solutions (Figure 4). The relaxation curve exhibited simple exponential behavior over all experimental conditions; its amplitude was wavelength dependent, corresponding to the absorption spectrum of Cr-(pyzH)$^{3+}$ ion. The time constant (τ) was dependent upon reactant concentrations, acidities, and temperature but invariant with the wavelength of the monitoring light. A delay of 50–100 ms between the time that flow stopped and temperature jump was applied was generally used; this interval was sufficient to ensure equilibration of Cr^{2+} and pyrazine but negligible bleaching of Cr(pyzH)$^{3+}$ ion. The data were fitted to (Scheme I) for which, under the experimental conditions

$$\tau^{-1} = k_f([Cr^{2+}]_e + [pyz']_e) + k_r \qquad (4)$$

with

$$k_f = (K_a K_1'' k_a' + k_1)/(1 + K_a/[H^+])$$

$$k_r = k_{-1} + k_{-a}'$$

$$K_1'' = [Cr(pyz)^{2+}]/[Cr^{2+}][pyz]$$

and other constants are as previously defined. The subscript e indicates concentrations are the equilibrium values. Derivation of the rate law is given in the Appendix.

Approximately equal concentrations of Cr^{2+} and pyrazine were used in the studies; reagent concentrations were varied over the ranges 0.04–2.5 mM, with [H$^+$] = 0.003–0.10 M and T = 11.4–28.1 °C. Results at 20.5 °C, which are typical, are given in Figure 5. Data analysis was based upon four to six individual determinations for each run; in general, standard deviations in τ were within 5% and never more than 10%. The constants k_f, k_r, and K_1' were determined by an iterative program of cycling through a weighted least-squares calculation of k_f and k_r based upon eq 4 using an assumed value for K_1', followed by correction for [Cr^{2+}]$_e$ and [pyz']$_e$ using the new value of K_1' determined from the rate constants. The process was repeated until convergence was obtained. In this way, evaluation of the kinetic data was made independently of the equilibrium binding studies; the values for K_1' deter-

Table I. Kinetic Constants for Cr(pyzH)$^{3+}$ Ion Formation

T, °C	slope,[a] 10^8 M^2 s	intercept,[a] 10^7 M s	a,b 10^{-6} M^{-1} s^{-1}	b,c M^{-1}	$|r|^d$
11.4 ± 0.4	13.5 ± 0.7	0 ± 1	1.5		0.995
20.5 ± 0.3	9.8 ± 0.9	2 ± 2	2.0	~0.5	0.976
28.1 ± 0.3	5.5 ± 0.3	−1.8 ± 0.6	3.6		0.933

[a] k_f^{-1} vs. [H$^+$]$^{-1}$. [b] $a = K_a$/slope $= K_a K_1'' k_a' + k_1$, calculated by using $K_a = 0.2$. [c] b = slope/intercept $= K_a$. [d] $|r|$ = weighted least-squares correlation coefficient.

mined by the two methods were identical within experimental error. Correlation coefficients for the plots according to eq 4 were $|r|$ = 0.954–1.00.

The hydrogen-ion dependence of k_f fits the functional form of eq 2, where, again, according to the proposed mechanism, slope/intercept ratios of plots of k_f^{-1} vs. [H$^+$] give K_a. The data are summarized in Table I; the intercept error is large, giving rise to large uncertainty in K_a. Within this error, however, K_a appears consistent with directly measured values. Also consistent with the proposed mechanism, k_r is pH independent (Figure 5); experimental values obtained are 62 ± 16, 154 ± 7, and 315 ± 30 s^{-1} at 11.4, 20.5, and 28.1 °C, respectively.

Analysis of the temperature dependence of the relaxation curves using the Eyring equation gave $\Delta H^{\ddagger}$ = 8.2 ± 3 kcal/mol, $\Delta S^{\ddagger}$ (20.5 °C) = −2 ± 10 eu for the Cr^{2+}–pyzH$^+$ association step(s), i.e., for $a = K_a K_1'' k_a' + k_1$ (Table I), and $\Delta H^{\ddagger}$ = 15.9 ± 0.7 kcal/mol, $\Delta S^{\ddagger}$ (20.5 °C) = 5.9 ± 2.4 eu for dissociation, i.e., $k_{-1} + k_{-a}'$. The plots are linear within experimental error with $|r|$ = 0.961, 1.00, respectively.

The rate law for pyrazine reduction of Cr(pyzH)$^{3+}$ ion was determined from the initial rates of bleaching in the presence of excess pyrazine to be

$$-d[Cr(pyzH)^{3+}]/dt = k_2'[Cr(pyzH)^{3+}][pyz']$$

At 20.6 °C, μ = 0.10 M, k_2' = 8.1 ± 1.6, 4.4 ± 0.8, and 0.74 ± 0.2 M^{-1} s^{-1} for [H$^+$] = 0.10, 0.04, and 0.01 M, respectively. Measured initial rates were corrected approximately for the slow decomposition of radicals by subtracting the residual bleaching rate after equilibration of the fast step in the biphasic curves had been reached. With the data base used, the magnitude of this correction was less than 10% of the overall initial rates. Reagent concentration ranges [Cr(pyzH)$^{3+}$] = 0.15–0.7 mM and [pyz'] = 0.4–3.0 mM were used.

The constant k_2' increases with increasing acidity. On the assumption that pyzH$^+$ is the reactive form of free pyrazine, i.e.

$$Cr(pyzH)^{3+} + pyzH^+ \xrightarrow{k_2} pyzH_2^+ + Cr(pyz)^{3+}$$
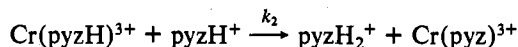
the relationship between k_2' and [H$^+$] would again be given by eq 2, where now $a = k_2$. Double reciprocal plots were not sufficiently accurate to determine the fundamental constants because of uncertainties in the intercept, but k_2 was estimated from K_a/slope, using K_a = 0.2 M, to be $k_2 \simeq$ 14 M^{-1} s^{-1} at 20.6 °C, μ = 0.10 M. Since $K_2 = k_2/k_{-2}$, it follows that $k_{-2} \simeq$ 10 M^{-1} s^{-1}.

Transient Kinetic Studies of Chromous Ion Reduction of A$_5$Co(pyz) Ion. A transitory green species was observed when solutions of chromous and A$_5$Co(pyz) ions were mixed; unlike the Cr(pyzH)$^{3+}$ ion, this intermediate decays within a second after mixing ($t_{1/2} \simeq$ 100 ms). Its visible absorption spectrum was determined from amplitudes of initial displacements of stopped-flow traces taken at various wavelengths (Figure 1); except for an increase in absorbance in the near-UV (300–350 nm) at higher acidities, the spectral intensities are acid independent over the range pH 1.0–2.0. Strong background
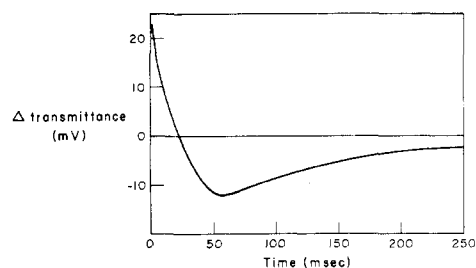
Figure 6. Oscilloscope trace of stopped-flow kinetic curves for chromous ion reduction of $A_5Co(pyz)$ ion at $[Cr]_T = [A_5Co(pyz)]_T = 1.0$ mM, $[H^+] = 0.01$ M, $\mu = 0.10$ M, 0 °C, and monitoring wavelength = 575 nm. Zero relative transmittance corresponds to the trace of the final product solution.

absorption by the $A_5Co(pyz)$ ion prevents measurement in the UV region.

It is apparent from the stopped-flow results that the redox reaction does not correspond to simple formation and decay of a single reaction intermediate. In regions of strong absorption, intermediate decay is preceded by a short induction period and at wavelengths where the green species is only weakly absorbing, formation of a second chromophore can be observed (Figure 6); this species forms at a rate which is 10^2-fold slower than that for formation of the green $A_5Co(pyz)Cr^{5+}$ ion, yet 10-fold faster than its decay.

Temperature-jump perturbation of solutions containing Cr^{2+} and $A_5Co(pyz)$ ions, when applied a few milliseconds after mixing, gave a single relaxation curve similar to that obtained for the $Cr(pyzH)^{3+}$ ion, although the time constant was 2 orders of magnitude greater in this instance. Maximum amplitudinal displacements were obtained at wavelengths where the green intermediate absorbed strongly. Increasing the time delay between mixing and perturbation resulted in loss of relaxational amplitudes, until at several hundred milliseconds delay no relaxation effect could be detected; loss of response corresponds to bleaching of the major chromophore. The time constant (τ) was independent of monitoring wavelength and, unlike $Cr(pyzH)^{3+}$, independent of acidity (over the range pH 1.0–2.0) and of reactant concentrations (over the ranges 0.5–4.0 mM). Measurements were generally made on solutions containing nearly equimolar reactant concentrations; at 7 °C, with $\mu = 0.1$ M, $\tau = 122 \pm 9$ μs.

Discussion

Composition and Electronic Structure of the Green Complex Ions. $Cr(pyzH)^{3+}$ Ion.

All kinetic and thermodynamic data indicate that formation of the green complex ion involves coordination of both chromous ion and a proton. It is reasonable to suppose that both ligand nitrogen atoms act as basic sites.

Several lines of evidence indicate that formation of the green ion involves more than simple substitution on chromous ion.

First, the stability of the ion is considerably greater than expected for simple ligand association (compare $K_1 = 1.5 \times 10^4$ M^{-1}, with the Ni^{2+}–pyrazine association constant,[20] $K = 10$ M^{-1}, under similar conditions). Furthermore, the $Cr(II)$ reaction requires ligand protonation, which should serve to decrease its metal-binding capabilities if the process were merely substitution. No evidence for binding of pyrazinium or N-methylpyrazinium ions to Ni^{2+} could be found under conditions where Ni^{2+}–pyrazine association is extensive.[20]

Second, the rate of formation of $Cr(pyzH)^{3+}$ ion appears to be too slow to be attributed to rate-limiting ligand substitution. The general mechanism given in Scheme I recognizes the indistinguishability of two pathways, namely, protonation preceding or following $Cr(II)$ substitution. The absence of

significant curvature in Eyring plots of the temperature dependence of the rate constants indicates only that either one of the pathways is predominant or that they have similar activation parameters. Nonetheless, an upper limit for $pyzH^+$ ion substitution on $Cr(II)$ can be set. From Table I, with $a = K_aK_1''k_a' + k_1 \geq k_1$ it follows that $k_1 \leq 3.6 \times 10^6$ M^{-1} s^{-1} at 28 °C. An estimate of the ligand substitution rate can be had by using the Eigen–Tamm formulation;[21] i.e., $k = K_{os}k_{ex}$, where K_{os} is the metal–ligand outer-sphere association constant and k_{ex} is the rate constant for water exchange on chromous ion, generally taken to be $k_{ex} \simeq 7 \times 10^9$ s^{-1}.[22] The magnitude of K_{os} was estimated from the equation $10^3K_{os} = \frac{4}{3}\pi a^3 N^\circ \exp(z_M a_L e_o^2/a'\epsilon kT)$,[23] where a is the distance between metal and ligand centers, a' is the distance between centers formally bearing the electrostatic charges, and the other constants have their usual meanings. From crystallographic data, we take $a = 4.85$ Å and $a' = 6.01$ Å, giving $K_{os} = 0.027$ M^{-1} and, therefore, $k \simeq 1.9 \times 10^8$ M^{-1} s^{-1}. The rate of formation of the green species is therefore about 10^2-fold slower than that anticipated for rate-limiting ligand substitution.[24]

Third, it is difficult to account for the spectral parameters of $Cr(pyzH)^{3+}$ ion, assuming that the metal ion is divalent. In particular, the near-ultraviolet band has an intensity and shape consistent with charge-transfer origin (Figure 1); it cannot be attributed to internal transitions on the ligand or reduced pyrazine radical ions.[19] The 30–40-nm bathochromic shift in the absorption maximum when the A_5Co moiety is substituted for a proton (vide infra) is consistent with ligand-to-chromium but not chromium-to-ligand charge transfer, since the proton is expected to be more effective than the cobalt(III) center in lowering ligand orbital energies.[26]

The data are consistent with formulation of $Cr(pyzH)^{3+}$ as a chromium(III)–pyrazine radical anion complex which, like the dihydropyrazine radical cation, is stabilized by protonation of available nitrogen sites and whose formation involves rate-limiting electron transfer associated with a modest activation energy ($\Delta G^\ddagger \simeq 9$ kcal/mol).

The $Cr(pyzH)^{3+}$ ion is EPR silent, suggesting strong spin coupling between unpaired electrons on the ligand radical and metal; signals from d^2 and d^4 systems are generally difficult to detect both because spin-orbit coupling is large and spin-lattice relaxation times are short.[27] In view of this result, it would seem appropriate to reexamine claims for formation of ligand radical intermediates based upon EPR evidence in re-

(21) Eigen, M.; Tamm, K. *Z. Elektrochem.* **1962**, *66*, 107.
(22) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 152.
(23) Rohrabacher, D. B.; Turan, T. S.; Defever, J. A.; Nichels, W. G. *Inorg. Chem.* **1969**, *8*, 1498.
(24) Similar arguments, though erroneous, have been advanced in a related system involving Cr(II) ligation of (pyrazine)carboxamide.[25] Here the authors have stated that, since aquation of the ligand is about 10^{10}-fold slower than the rate of water exchange on Cr(II), some process other than substitution must be rate limiting. However, the reaction is energetically unfavorable and therefore not at all inconsistent with rate-limiting ligand substitution. Interestingly, the rate constant for formation of the green chromium–(pyrazine)carboxamide complex was estimated at 2×10^6 M^{-1} s^{-1} at 25 °C, $[H^+] = 1.0$ M, nearly identical with the upper limit for k_1 in our system. Although the acid dependence of the reaction was not studied, kinetic analysis along the lines described above can be expected to give a similar conclusion, i.e., that ligand substitution on Cr(II) ion is not rate limiting.
(25) Wu, M. Y.; Paton, S. J.; Fanchiang, Y. T.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.
(26) The nature of the 637-nm absorption band in the $Cr(pyzH)^{3+}$ and $A_5Co(pyz)Cr^{5+}$ ions is presently unclear. Both the narrow band width and independence of substituent at the remote nitrogen atom are inconsistent with charge-transfer excitation. Quite similar bands have been observed in Cr(II) reactions with other substituted pyrazines[5,6] but not in reactions involving other reducing metal ions.[25] One possibility is that the band originates from a metal-centered d–d transition which is intensified by mixing with ligand radical orbitals.
(27) McGarvey, B. R. "Transition Metal Chemistry"; Dekker: New York, 1966; Vol. 3, p 90.

(20) Malin, J. M.; Shepherd, R. E. *J. Inorg. Nucl. Chem.* **1972** *10*, 109.

actions of Cr(II) with substituted pyrazines[25] and their A_5Co complexes;[8] specifically, radical–ion equilibration processes analogous to eq 3 have not been considered, but formation of free organic radicals might well account for observed EPR signals in these reactions.

$A_5Co(pyz)Cr^{5+}$ Ion. The spectral similarity to $Cr(pyzH)^{3+}$ ion suggests that the green transient comprises pyrazine radical anion coordinated to Cr(III) and Co(III) metal centers; in particular, the appearance of the 637-nm band implicates Cr(III) coordination,[26] and the absence of any dependence upon acidity as well as the spectral shift in the 400-nm band indicates that the remote nitrogen position is still occupied by cobalt.

Kinetic Complexities in Cr^{2+} Ion Reduction of $A_5Co(pyz)^{3+}$ Ion. A cursory analysis of the stopped-flow data would suggest straightforward interpretation of the reaction, with Cr^{2+} binding followed by stepwise electron transfer to ligand and then, more slowly, from ligand to Co(III). Disappearance of the transitory green species occurs at least 10^3-fold faster than for the $Cr(pyzH)^{3+}$ ion in a pH-independent step, consistent with expectations for intramolecular electron transfer to a bound oxidant center; spectral analysis suggests that the major chromic product contains bound pyrazine.[8] Furthermore, a relaxation qualitatively similar to that identified as reversible binding of Cr(II) to pyrazine is found when Cr(II) and Co-(pyz) ions are rapidly mixed and perturbed.

However, detailed analysis of both stopped-flow (Figure 6) and relaxation data indicate that this simple mechanism is inadequate. The relaxation time constant does not fit the functional form expected for reversible bimolecular ion formation (eq 4) but rather is concentration independent. Assignment to a unimolecular process such as reversible electron transfer in the binuclear ion, i.e., the second step of the equilibrium

$$A_5Co(pyz) + Cr(II) \rightleftharpoons A_5Co(pyz)Cr^{II} \rightleftharpoons A_5Co(pyz)Cr^{III}$$
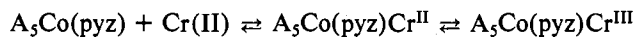
appears untenable since, under the experimental conditions, the $A_5Co(pyz)Cr^{II}$ binuclear ion is almost certainly present in only vanishingly small concentrations[20] and, therefore, requires that the time constant exhibit concentration dependence. Likewise, the possibility seems remote that the apparent concentration independence arises from only very weak association of Cr(II) and $A_5Co(pyz)$ ions to give an intensely absorbing intermediate, which would result in dominance of the concentration-independent term in eq 4. Measurements of spectral intensities of the green transient initially formed suggest that significant association occurs under the experimental conditions, with $K = [A_5Co(pyz)Cr^{5+}]/[Cr^{2+}][A_5Co(pyz)^{3+}] \approx 10^2 M^{-1}$. The pH independence of the relaxation indicates that protic equilibria are not involved.

Although the relaxation does not yet yield to simple interpretation, it is clearly not due to equilibration of Cr(II) with free pyrazine (which might be formed by rapid electron transfer between Cr(II) and $A_5Co(pyz)$); the time constant is 10^2-fold greater than that for $Cr(pyzH)^{3+}$ ion and, as noted, is pH independent. It should also be emphasized that, in contrast to the $A_5Co(pyz)-Cr^{II}$ reaction, no evidence for the existence of isomeric 1:1 complexes between Cr(II) and pyrazine could be found.

Appendix

The general solution to the rate law for Scheme I gives three roots. Protic and chromous ion ligation equilibria, represented by $K_a = k_{-a}/k_a$ and $K_1'' = k_1''/k_{-1}''$, respectively, occur at immeasurably rapid rates under the experimental conditions, so that only a single relaxation is observed.

The rate law is

$$d[Cr(pyzH)^{3+}]/dt = k_1[Cr^{2+}][pyzH^+] +$$
$$k_a'[Cr(pyz)^{2+}][H^+] + (k_{-1} + k_{-a}')[Cr(pyzH)^{3+}]$$

Expressing concentrations in terms of the sums of their equilibrium concentrations and their displacements from equilibria, e.g., $[Cr^{2+}] = [Cr^{2+}]_e + \delta(Cr^{2+})$, and assuming hydrogen-ion buffering, i.e., $\delta(H^+) \simeq 0$, which is valid in the highly acidic solutions used, one obtains the rate law

$$d(\delta(Cr(pyzH)^{3+}))/dt =$$
$$k_1([Cr^{2+}]_e\delta(pyzH^+) + [pyzH^+]_e\delta(Cr^{2+})) +$$
$$k_a'[H^+]\delta(Cr(pyz)^{2+}) - (k_{-1} + k_{-a}')\delta(Cr(pyzH)^{3+}) \quad (1)$$

where, as usual, higher order differential terms have been ignored.[28] Introducing the conservation equations

$$\delta(Cr^{2+}) + \delta(Cr(pyz)^{2+}) + \delta(Cr(pyzH)^{3+}) = 0 \quad (2)$$

$$\delta(Cr^{2+}) = \delta(pyz) + \delta(pyzH^+) \quad (3)$$

and the "uncoupled" equilibrium approximations

$$\delta(pyz) = (K_a/[H^+])\delta(pyzH^+) \quad (4)$$

$$\delta(Cr(pyz)^{2+}) = K_1''([Cr^{2+}]_e\delta(pyz) + [pyz]_e\delta(Cr^{2+})) \quad (5)$$

we obtain

$$d(\delta(Cr(pyzH)^{3+}))/dt = -\delta(Cr(pyzH)^{3+})/\tau$$

where

$$\tau^{-1} = (k_a'[H^+] + k_1[H^+]/K_aK_1'')/(1 + \{[K_1''/(1 + [H^+]/K_a)][[pyz']_e + [Cr']_e/(1 + K_1''[pyz']_e/(1 + [H^+]/K_a))]\}^{-1}) + k_{-1} + k_{-a}' \quad (6)$$

with $[Cr']_e = [Cr^{2+}]_e + [Cr(pyz)^{2+}]_e$ and other constants as previously defined. On the basis of measured association constants for pyrazine binding to other divalent transition-metal ions,[20] it is anticipated that the $Cr(pyz)^{2+}$ ion is present at only very small concentration levels. With this assumption, i.e., $[Cr(pyz)^{2+}]_e \ll [Cr^{2+}]_e$ and, therefore, that $[Cr(pyz)^{2+}]_e \ll [pyz']_e$, where under our experimental conditions $[pyz]_e \geq [pyzH^+]_e$ and $[pyz']_e \approx [Cr']_e$, it follows that $K_1''[pyz']_e \approx K_1''[Cr']_e \ll 1$, and eq 6 reduces to eq 4 in the text.

By detailed balancing, it also follows that

$$K_1' = K_1/(1 + K_a/[H^+])$$

(28) Eigen, M.; DeMaeyer, L. *Tech. Org. Chem.* **1963**, *8*, 895.