450 °C. Extensive THF cleavage was observed in the temperature range 90–220 °C.

When CH_3Li was allowed to react with MgH_2 in a 2:1 ratio in THF, a clear solution resulted. Elemental analysis indicated the empirical formula $Li_2MgH_2Me_2$. The ^1H NMR spectrum of this solution at room temperature exhibited one singlet at 3.62 ppm upfield from the THF multiplet. Only one singlet due to methyl protons was found, even at −80 °C. Reaction of this solution with $LiAlH_4$ (eq 14) produced a highly gelatinous precipitate which was hard to filter. This precipitate when dried under vacuum gave a white solid whose elemental analysis corresponded to Li_2MgH_4. This compound did not exhibit an x-ray powder pattern because of its amorphous nature. The filtrate of the reaction mixture showed Al–H stretching at 1675 cm^{-1} characteristic of $LiAlH_2Me_2$ in THF.

$$Li_2MgH_2Me_2 + LiAlH_4 \rightarrow Li_2MgH_4 + LiAlH_2Me_2 \qquad (14)$$

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Registry No. $LiAlH_4$, 16853-85-3; MgH_2, 7693-27-8; Me_2Mg, 2999-74-8; Et_2Mg, 557-18-6; Bu_2Mg, 1191-47-5; Ph_2Mg, 555-54-4; MeMgH, 63533-51-7; EtMgH, 63533-53-9; BuMgH, 65015-67-0; PhMgH, 62086-01-5; MeLi, 917-54-4; EtLi, 811-49-4; BuLi, 109-72-8; PhLi, 591-51-5; $LiMgHMe_2$, 65015-95-4; $LiMgHEt_2$, 65015-94-3; $LiMgHBu_2$, 65015-93-2; $LiMgHPh_2$, 65015-92-1; $Li_2MgH_2Me_2$, 65015-91-0; Li_2MgH_4, 65015-90-9; $LiMg_2H_3Bu_2$, 65101-99-7; $LiMg_2H_5$, 65104-00-9; $LiMgPh_3$, 65015-89-6; Li_3AlH_6, 16941-14-3; $LiMgH_3$, 65015-88-5; $LiMgH_2Ph$, 65015-87-4; $LiAlH_2Ph_2$, 27662-04-0; $LiAlHPh_3$, 62126-58-3; $LiMgH_2Me$, 65015-86-3; $LiMgDMe_2$, 65015-85-2; LiH, 7580-67-8; $LiAlH_2Me_2$, 19528-78-0; $LiAlH_2Et_2$, 25897-84-1; $LiAlH_2Bu_2$, 65015-84-1; $LiAlH_3Ph$, 65058-51-7.

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Electron Transfer. 30. Chromium(III)-Bound Pyrazine Radicals[1]

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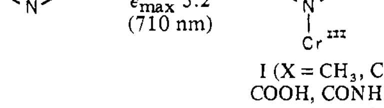
The pyrazine greens are strongly absorbing species (λ_{max} 645–650 nm, $\epsilon < 10^3$) formed by the action of Cr^{2+} on substituted pyrazines in aqueous acidic solution. The reactions of one of the most stable of these, derived from pyrazinecarboxamide, with a number of $(NH_3)_5Co^{III}$ complexes yield Co^{2+}, together with the same Cr(III) product as is formed in reduction by Cr^{2+} itself, but rates are several orders of magnitude lower. Such reactions are further inhibited by excess amide. Kinetic data support sequence 2, in which the green radical cation, formulated as $Cr^{III}Pz\cdot$, dissociates (k_1) to the parent pyrazine and Cr^{2+}, which, in turn, may react with Co(III) (k_2) or return to the radical cation (k_{-1}). Values of k_1/k_{-1} obtained from measurements on different Co(III) systems are in agreement, and k_2 values for the reactions of fluoro- and bromopentaamminecobalt(III) complexes with Cr^{2+} are consistent with literature rates. The calculated rate of dissociation of the green ion to Cr^{2+} is 10^{10}–10^{11} times lower than the accepted range for substitution reactions at Cr(II) centers but several orders of magnitude above the heterolysis rates of the usual Cr(III) complexes in water, suggesting that the rate of dissociation is determined by the rate of internal electron transfer within the radical cation. The equilibrium constant for the conversion of $Cr^{III}Pz\cdot$ to Cr^{2+} is found to be one-tenth of that estimated from the reduction potentials of Cr^{3+} and pyrazinecarboxamide, indicating that $Cr^{III}Pz\cdot$ is 10 times as stable toward aquation as is the pyrazinecarboxamide complex of Cr(II).

In 1965 it was reported[2] that the reaction of Cr^{2+} with pyrazine derivatives very rapidly yielded intensely absorbing green species displaying spectra quite unlike those of hydrated or partially hydrated Cr(II) or Cr(III). Because these "pyrazine greens" are not formed by the action of other reducing agents (e.g., Eu^{2+}, V^{2+}, U^{3+}, or zinc amalgam) and because they react readily with such one-electron oxidants as $(NH_3)_5CoCl^{2+}$, the proposal was made that they are chromium(III)-bound radicals (I), each featuring a reduced pyrazine ring, a suggestion which has been strengthened by the finding[3] that several of these materials exhibit ESR signals that can reasonably be attributed neither to Cr(II) nor to Cr(III). These ions, which have been prepared from a variety of substituted pyrazines and from fused-ring pyrazines (quinoxaline and phenazine), exhibit a considerable range of stabilities in aqueous solution. Some decompose in a few seconds, whereas others can be kept for almost 1 h under favorable conditions and can thus be studied using conventional mixing techniques.



I ($X = CH_3$, Cl, COOH, $CONH_2$)
$\epsilon_{max} > 10^3$
(648 nm)

Since these bound radicals are presumed to be structurally similar to a number of substituted-pyridine radicals which have been implicated[4] as the active intermediates in a series of reductions of bound cobalt(III) with Cr^{2+} and Eu^{2+} as catalyzed externally by certain 4-substituted pyridines, it might be anticipated that they would be much more facile reductants than these hydrated metal centers. The reverse is the case. Their oxidations by the most reactive cobalt(III) complexes have been found to be several orders of magnitude slower (under comparable conditions); hence, stoichiometric quantities of pyrazines, when added to Cr(II)–Co(III) systems, effectively retard electron transfer to the Co(III) center.

The present communication deals principally with reductions by one of the more stable of the pyrazine greens, that derived from pyrazinecarboxamide (I, X = $CONH_2$). We here present evidence that the reducing properties of this pigment may be attributed almost exclusively to the small concentration of Cr^{2+}(aq) in equilibrium with it.

Experimental Section

Materials. Solutions of $Cr(ClO_4)_2$ were prepared and analyzed as described.[2a] Chloro-, bromo-, and fluoropentaamminecobalt(III) salts were prepared by literature procedures;[5] the chloro dichloride was converted to the corresponding perchlorate with aqueous $HClO_4$,[6a] the bromo dibromide to its perchlorate with concentrated $HClO_4$,[6b] and the fluoro dinitrate to its perchlorate by dissolving in water and adding saturated $NaClO_4$. The analogous iodo perchlorate was prepared by the method of Haim and Taube.[7] Heterocyclic cobalt(III) perchlorates were available from a previous study.[8] Substituted pyrazines were Aldrich products and were used as received. All reactions involving Cr^{2+} or chromium(II)–pyrazine preparations were carried out under nitrogen.

Preliminary Observations. The chromium(II)–pyrazine products in this study were conveniently generated by mixing solutions of $Cr(ClO_4)_2$ and the substituted pyrazine, both in 1 M $HClO_4$. When such an addition was carried out under stop-flow conditions with $[Cr^{2+}] = 0.001$ M and pyrazinecarboxylic acid in tenfold excess, formation of the green color was found to be at least 95% complete within the time of mixing (0.005 s). Spectrophotometric titration of this carboxylic acid and its amide with Cr^{2+} indicated a 1:1 ratio of reactants; the product from the acid exhibited an absorption maximum at 648 nm (ϵ 1.0×10^3) and that from the amide exhibited one at 645 nm (ϵ 1.1×10^3). As excess Cr^{2+} was added to these preparations, a new peak appeared near 625 nm; this peak became predominant when $[Cr^{II}]/[\text{ligand}]$ exceeded 10. The second absorbance, which was observed also with 2,3-pyrazinedicarboxylic acid and with its diamide but not with unsubstituted pyrazine, probably reflects formation of a ligand–2Cr(II) adduct. This species appears to play no part in the redox reactions studied. Green products of this type were not formed from pyrimidine derivatives.

For ESR measurements, using a Varian V-4500 X-band spectrometer, 0.01–0.05 M solutions of several of the green species were prepared in 90% aqueous ethanol which was also 1.0 M in $HClO_4$. Each of the materials exhibited a signal near $g = 2.0$, but the breadth of the absorption appeared to be strongly and, at present, unaccountably dependent on the nature of the ring substituents and, in some cases, on whether Cr^{2+} or the heterocycle was taken in excess. The approximate peak-to-peak width for the phenazine complex was 15 G, that for the complex of unsubstituted pyrazine 30 G, and that for pyrazinecarboxamide (with the amide in excess) 24 G ($g = 1.96$). With Cr^{2+} in excess, the pyrazinecarboxamide signal broadened to 200 G. The preparation from pyrazinecarboxylic acid (with the acid in excess) featured an intense overlapping eight-line signal centered at $g = 1.99$, but with Cr^{2+} in excess, only a single line ($g = 1.96$) was evident. Under these conditions $Cr(ClO_4)_3$ solution in the absence of pyrazine exhibited weak absorbance (width 190 G at $g = 1.96$), whereas $Cr(ClO_4)_2$ displayed no signal.

Each of the pyrazine greens reacted readily with the various halopentaamminecobalt(III) complexes, yielding Co^{2+}, and with the $(NH_3)_5Co^{III}$ derivatives of 4-acetylpyridine (II), 4-benzoylpyridine (III), and pyrazine (IV). Reactions with the maleato, pyruvato, formato, and *N*,*N*-diethylnicotinamide derivatives of $(NH_3)_5Co^{III}$ were slow, and simple kinetic curves could not be obtained, due, in large part, to competing changes in the green pigments not involving Co(III).

Rate Measurements. Rates of redox reactions featuring the most stable of the green ions, that derived from pyrazinecarboxamide ($PzCONH_2$), were estimated from measurements of absorbance decreases on a Cary 14 recording spectrophotometer. To minimize complications arising from unreacted Cr^{2+} and from the species absorbing at 625 nm, mentioned in the preceding section, reactions were carried out with $[PzCONH_2]/[Cr^{2+}] > 4$. Measurements were made near 645 nm or at the low-energy maximum of the Co(III) oxidant used. All reactions were first order in the green species (hence first order in added Cr^{2+}). Oxidations by the heterocyclic $(NH_3)_5Co^{III}$ derivatives were first order in Co(III), but those by the halopentaamminecobalt(III) complexes exhibited a more complex Co(III) dependence. Reactions were inhibited by excess $PzCONH_2$. Rate measurements were generally made under pseudo-first-order conditions with Co(III) in excess; when Co(III) was in deficiency, slow decomposition of the green ion complicated interpretation of the absorbance changes. The supporting electrolyte was 1.0 M $HClO_4$. Reactions were generally followed for at least 4 half-lives and pseudo-first-order rate constants calculated from logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Table I. Stabilities of Pyrazine Greens

Heterocyclic base	Reducing power recovered, %[a]
Chloropyrazine	38
Pyrazinetetracarboxylic acid	52[b]
2,3-Pyrazinedicarboxylic acid	59
Methylpyrazine	61
2,6-Dimethylpyrazine	76
Pyrazinecarboxylic acid	77
Pyrazine	84
2,5-Dimethylpyrazine	88
2,6-Dichloropyrazine	93
Quinoxaline	99
	100[c]
	100[d]
Pyrazinecarboxamide	100
	100[c]
	100[d]

[a] 0.033 mmol of base and 0.030 mmol of Cr^{2+} in 1.5 mL of 1.2 M $HClO_4$. Waiting period 30 s unless otherwise indicated (see text). [b] Green color quickly faded; amber precipitate formed. [c] Waiting period 20.5 min. [d] 0.150 mmol of base used. Waiting period 30 s.

Comparison of Stabilities. Approximate comparison of the stabilities of the various pyrazine greens was carried out by allowing solutions to stand for a known time period, adding $(NH_3)_5CoCl^{2+}$, and then estimating the fraction of reducing power retained by measuring the quantity of Co^{2+} released. Samples (0.033 mmol) of substituted pyrazines were dissolved in 1.5 mL of 1.2 M $HClO_4$, nitrogen was bubbled through the solutions to remove O_2, 0.030 mmol of $Cr(ClO_4)_2$ was added, and, after a measured waiting period, a saturated solution of $(NH_3)_5CoCl(ClO_4)_2$ was added through the cap (syringe) until the maroon color of the Co(III) complex persisted. The sample was then uncapped and diluted to 25.0 mL with concentrated HCl, the absorbance at 692 nm was read, and the number of moles of Co(II) produced was calculated.[2a] Results are summarized in Table I.[9] The green species were generally much less stable in 0.1 M than in 1.2 M $HClO_4$; the manner in which they decompose was, however, not determined. Such decompositions appeared to be no more rapid in direct sunlight than in the dark.

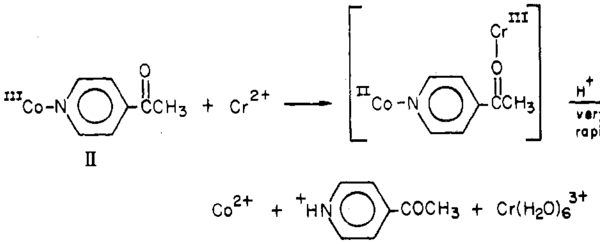
Ion-Exchange Experiments. To a solution containing 0.03–0.05 mmol of $Cr(ClO_4)_2$ and a measured quantity of $PzCONH_2$ in 5 mL of 1.2 M $HClO_4$ was added a quantity of dissolved Co(III) oxidant equivalent to the Cr^{2+} taken. Reactions were allowed to proceed for about 30 min, after which the mixtures were subjected to cation-exchange chromatography (Bio-Rad, 50W-X2, 200–400 mesh).

Separations were run at 25 °C as described,[10] using about 6 cm^3 of resin comprising a 15-cm column; the elution rate was 0.5 cm^3/min. Complete separations generally required less than 90 min. After removal of Co^{2+}, the Cr(III) product was eluted as a single band, followed, in some cases, by a small quantity of the unreacted Co(III) oxidant. With $(NH_3)_5CoCl^{2+}$, the sole Cr(III) product was $(H_2O)_5CrCl^{2+}$, whereas with the 4-acetylpyridine derivative of $(NH_3)_5Co^{III}$ as oxidant, only $Cr(H_2O)_6^{3+}$ was obtained. The spectrum of each of these products and the extent to which each was recovered from the resin (85–93%) corresponded closely to those observed when the respective Co(III) complex was reduced by Cr^{2+} in the absence of dissolved pyrazinecarboxamide. The products did not change when the $[PzCONH_2]/[Cr^{2+}]$ ratio was increased from 1 to 10.

Results and Discussion

It has long been known that the Cr^{2+} reduction of

$(NH_3)_5CoCl^{2+}$ yields $(H_2O)_5CrCl^{2+}$ quantitatively.[11] Identification of the same chlorochromium(III) cation as the sole Cr(III) product from reaction of this oxidant with the $PzCONH_2$–Cr(II) species, even when the amide is in tenfold excess, may be taken as very strong evidence that Cr^{2+} is the only significant reducing species in the latter system. In particular, we may rule out direct reduction by either a chromium(III)-bound radical or a chromium(II)–pyrazine complex, for, in either case, the organic group would be expected to remain bound to the Cr(III) product.[2] With the 4-acetylpyridine complex II as oxidant, the green chromium(II)–amide species yields $Cr(H_2O)_6^{3+}$, which is also the Cr(III) product first detected when acylpyridine derivatives of $(NH_3)_5Co^{III}$ react with Cr^{2+} itself:[2b,8]



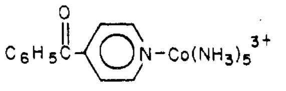
(1)

The acetylpyridine reaction is consistent with intervention of Cr^{2+} as the active reducing agent, but here the implication is somewhat less compelling, for $Cr(H_2O)_6^{3+}$ could conceivably be formed, at least in part, from the original reaction with pyrazinecarboxamide.

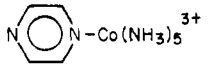
The marked inhibition of each of the $Cr(II)–PzCONH_2–Co(III)$ reactions by excess amide indicates a preliminary equilibrium in which the reactive reductant is formed, together with $PzCONH_2$, from the major chromium species in solution. Thus, qualitative observations alone point to the sequence 2

$$\begin{gathered}\mathrm{Cr^{III}Pz\cdot} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Pz} + \mathrm{Cr^{2+}} \\ \mathrm{Cr^{2+}} + \mathrm{Co(III)} \xrightarrow{k_2} \mathrm{Co^{2+}} + \mathrm{Cr^{III}}\end{gathered} \tag{2}$$

for the reductions of cobalt(III). In view of the extreme rapidity with which Cr^{2+} reacts with the halopentaamminecobalt(III) ions[12] and with the 4-acetylpyridine (II), 4-benzoylpyridine (III), and pyrazine (IV) oxidants used,[8] we



III



IV

may apply the steady-state approximation to this reductant and obtain rate law 3.

$$\text{rate} = \frac{-d[\mathrm{Co^{III}}]}{dt} = \frac{k_1k_2[\mathrm{Cr^{III}Pz\cdot}][\mathrm{Co^{III}}]}{k_{-1}[\mathrm{Pz}] + k_2[\mathrm{Co^{III}}]} \tag{3}$$

Kinetic data are summarized in Table II. Note that the reaction rates of the aromatic cobalt reagents II–IV are inversely proportional to the concentration of pyrazinecarboxamide. For these oxidants, the first term in the denominator of (3) is dominant, and the rate law assumes the monomial form (4). In these cases, plots of the observed

$$\text{rate} = \frac{k_1k_2[\mathrm{Cr^{III}Pz\cdot}][\mathrm{Co^{III}}]}{k_{-1}[\mathrm{Pz}]}$$

second-order specific rates vs. 1/[Pz] are linear with slope k_1k_2/k_{-1}, and from k_2 values already determined,[8] we may estimate K_1 ($=k_1/k_{-1}$), the equilibrium constant for Cr^{2+}–$Cr^{III}Pz\cdot$ interconversion, a ratio which should be independent of the Co(III) oxidant taken. Values of k_1/k_{-1} from the acetyl and benzoyl oxidants (Table III) are seen to be in agreement.

Our data for the cobalt(III)–pyrazine complex IV, in conjunction with K_1 derived from the acetyl and benzoyl systems, lead to a specific rate of 8.7×10^4 M^{-1} s^{-1} for the reduction of this complex by Cr^{2+} at $\mu = 1.0$. This is slightly less than the recorded value (1.0×10^5) at $\mu = 0.24$,[8] whereas one would expect a more rapid reduction at the higher ionic strength. Since the very rapid kinetic curves on which the earlier estimate was based required a time resolution near the performance limit of the instrument used and involved a relatively small absorbance change, we regard the present specific rate as more reliable.

Table II. Kinetic Data for Oxidation of the Chromium(III)-Bound Pyrazinecarboxamide Radical with Pentaamminecobalt(III) Complexes $R(NH_3)_5Co^{III}$

Co(III)-bound ligand R	λ, nm	$10^4[Cr^{III}$-$Pz\cdot]$	$10^3[PzCONH_2]$	$10^{-3}k_1$,[a] s^{-1}
4-Acetylpyridine (II)	475	1.0	0.50	12.8
		1.0	0.75	9.5
		2.0	1.00	7.2
		2.0	1.50	4.4
		2.5	2.00	3.6
		5.0	3.00	2.5
		5.0	4.00	1.6
4-Benzoylpyridine (III)	475	1.0	0.50	6.5
		1.0	0.75	5.0
		2.0	1.00	3.1
		2.0	1.50	2.4
		2.5	2.00	1.7
		5.0	3.00	1.20
		5.0	4.00	1.12
Pyrazine (IV)	475	1.0	0.50	12.6
		1.0	0.75	9.1
		2.0	1.00	6.3
		2.0	1.50	4.3
		2.5	2.00	2.9
		5.0	3.00	2.0
		5.0	4.00	1.64
Fluoro	510	1.0	0.50	33
		1.0	1.00	20
		2.0	1.50	14.4
		2.0	2.00	10.8
		2.5	2.50	9.6
		5.0	3.00	8.7
		5.0	4.00	6.2
		5.0	5.00	5.4
Chloro	532	1.0	0.50	50
		1.0	0.75	46
		2.0	1.00	43
		2.0	1.50	39
		2.5	2.00	30
		5.0	2.50	27
		5.0	3.00	23
		5.0	4.00	21
		1.0	1.00	41[b]
		1.0	1.00	28[c]
		1.0	1.00	22[d]
		1.0	1.00	53[e]
Bromo	550	1.0	0.50	63
		2.0	1.00	53
		2.0	2.00	41
		5.0	4.00	28
		5.0	10.0	15
Iodo	584	5.0	5.0	140
		5.0	15.0	120

[a] Pseudo-first-order rate constants at 25 °C. Supporting electrolyte was 1.0 M $HClO_4$. $[Co^{III}]_0$ was 2.5×10^{-3} M unless otherwise indicated. [b] $[Co^{III}]_0 = 2.0 \times 10^{-3}$ M. [c] $[Co^{III}]_0 = 1.25 \times 10^{-3}$ M. [d] $[Co^{III}]_0 = 1.00 \times 10^{-3}$ M. [e] $[Co^{III}]_0 = 4.0 \times 10^{-3}$ M.

Table III. Kinetic Parameters for the Oxidation of the Chromium(III)-Bound Pyrazinecarboxamide Radical with Pentaamminecobalt(III) Complexes $R(NH_3)_5Co^{III}$ [a]

$$Cr^{III}Pz\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pz + Cr^{2+} \xrightarrow[k_2]{Co^{III}} Co^{2+} + Cr^{III}$$

Co(III)-bound ligand R	k_1k_2/k_{-1} [b]	k_2	K_1 $(=k_1/k_{-1})$	k_1 [c]	k_{-1} [d]
4-Benzoylpyridine (III)	1.4×10^{-3}	4.8×10^{4} [c]	2.9×10^{-8}		
4-Acetylpyridine (II)	2.9×10^{-3}	9.7×10^{4} [e]	3.0×10^{-8}		
Pyrazine (IV)	2.6×10^{-3}	8.7×10^{4} [f]			
Fluoro	1.16×10^{-2}	4.1×10^{5} [f] 9×10^{5} [g]		0.060	2.0×10^{6}
Chloro	4.5×10^{-2}	1.6×10^{6} [f] 2.6×10^{6} [g]		0.063	2.1×10^{6}
Bromo	7.8×10^{-2}	2.7×10^{6} [f] 1.4×10^{6} [h]		0.073	2.4×10^{6}

[a] Temperatures 25 °C. Reactions were carried out in 1.0 M $HClO_4$ unless otherwise indicated. Values of k_{-1} and k_2 are in $M^{-1}\ s^{-1}$; values of k_1 are in s^{-1}. [b] Ratio obtained for oxidants II, III, and IV from plots of $k_{obsd}/[Co^{III}]$ vs. $[PzCONH_2]$, where k_{obsd} is the pseudo-first-order specific rate. Ratio obtained for the halo oxidants from the slopes of plots of $1/k_{obsd}$ vs. $[PzCONH_2]$ (see text and Figure 1). [c] Obtained from the intercepts of plots of $1/k_{obsd}$ vs. $[PzCONH_2]$ (see text and Figure 1). [d] From K_1 (taken as $3.0 \times 10^{-8}\ M^{-1}$), in conjunction with measured values of k_1. [e] See ref 8. [f] This work. [g] Reaction in 0.1 M $HClO_4$ + 0.9 M $NaClO_4$ (see ref 12). [h] Reaction in 0.1 M $HClO_4$ (see ref 12).

With the fluoro-, chloro-, and bromocobalt(III) oxidants, reactions are inhibited by excess pyrazinecarboxamide, but dependency is less steep than that corresponding to an inverse-first-order dependence. Here, neither term in the denominator of (3) can be ignored. In these instances, plots of $1/k_{obsd}$ vs. $[PzCONH_2]$ with $[Co^{III}]$ held constant are closely linear (Figure 1). Intercepts of the least-squares lines lead to values of k_1, the specific rate of collapse of the green radical cation I to Cr^{2+} and the parent pyrazine, whereas slopes of these lines, in combination with K_1 determined for the acylpyridine oxidants, lead to k_2, the Co^{III}–Cr^{2+} specific rates. Values of k_1 obtained from the three halocobalt(III) systems are, as expected, independent of the oxidant taken.[13]

Estimates of k_2 from this study are compared with those obtained directly by Candlin and Halpern[12] in Table III. Agreement for the bromo and fluoro oxidants may be taken to be reasonable when it is considered that our bromo value was obtained at considerably higher ionic strength and that our fluoro value refers to a more strongly acidic medium than was used by these workers.[14] Agreement for the chloro compound is less satisfactory; in view of the relatively narrow range of rates used in our determination, we tend to favor the earlier figure.

Limited data on the iodocobalt(III) oxidant indicate that the rate at which it is reduced in our systems is very nearly independent of $[PzCONH_2]$, thus suggesting for this halo complex the second term in the denominator of (3) is predominant and that the specific rate observed is simply k_1, describing the formation of Cr^{2+} from the green ion, a process which has now become rate determining. However, the observed iodo rate constants do not correspond to the extrapolated k_1 values for the other halo complexes but are approximately twice as large, pointing to the operation of a second mode of reduction (perhaps involving direct reaction of Cr^{III}–$Pz\cdot$) peculiar to this oxidant. Further investigation of this facet is desirable.

For the six remaining Co(III) oxidants, it is clear that direct action of the green ion plays a negligible part in the redox process even though this ion is present at about 10^4 times the concentration of Cr^{2+}. The inactivity of this ion is further evidence that it is a chromium(III)–radical complex rather than a (isomeric) chromium(II)–ligand species, for there appears to be no past instance in which the reactivity of Cr^{2+} is so drastically decreased by ligation, whether the donor be soft[15] or hard.[16]

Still more persuasive on this question is the observed magnitude for k_1 (0.07 s^{-1}), a value that falls below the accepted range for substitution reactions at Cr(II) centers[17] by a factor of 10^{10}–10^{11}. At the same time, the cleavage of Cr^{III}–$Pz\cdot$ is several orders of magnitude more rapid than the unimolecular heterolysis of partially aquated Cr(III) complexes under similar conditions.[18] We suspect then that the rate of dissociation of the radical ion is determined by the rate of internal electron transfer to form a Cr^{II}–$PzCONH_2$ complex,[19] which can then undergo a rapid (and reversible) heterolysis.

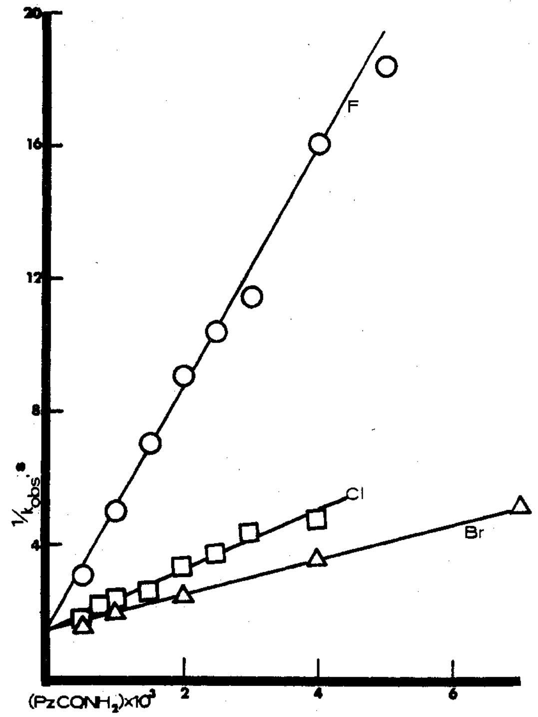


Figure 1. Rate data for the reactions of fluoro-, chloro- and bromopentaamminecobalt(III) complexes $(NH_3)_5CoX^{2+}$ with the chromium(III)-bound pyrazinecarboxamide radical Cr^{III}–$Pz\cdot$ at 25 °C, 1.0 M $HClO_4$. $[Co^{III}]_0$ = 0.0025 M for all runs shown. Reciprocals of the pseudo-first-order rate constants, k_{obsd}^{-1}, are plotted against the concentrations of pyrazinecarboxamide taken. Intercepts of the regression lines yield values of k_1^{-1} (see sequence 2 in text), whereas slopes equal $(K_1k_2[Co^{III}])^{-1}$. Kinetic parameters derived from these plots are listed in Table III.

Finally, it is of interest to compare K_1, referring to the interconversion of Cr^{III}–$Pz\cdot$ and Cr^{2+}, to the value predicted for a simple electron-transfer reaction, using standard

Cr^{3+}–Cr^{2+} and Pz–Pz· potentials in the medium taken. Measurements by Fanchiang and co-workers[20] point to an apparent reduction potential for pyrazinecarboxamide (in 1.0 M $HClO_4$) very nearly the same as that for pyrazine itself which, from the data of Klatt and Rouseff,[21] may be assigned a value −0.020 V (vs. NHE). This, in combination with a Cr^{3+} potential of −0.41 V,[22] leads to an equilibrium constant of 3×10^{-7} for a redox reaction uncomplicated by chromium–pyrazine coordination. The discrepancy between this value and the observed constant, 3×10^{-8} M, indicates that the chromium(III)–radical complex is 10 times as stable toward heterolysis under our reaction conditions as is the (unobservable) chromium(II)–pyrazine complex, but in the absence of further information we cannot assign individual formation constants to these isomeric species.

Registry No. Cr, 7440-47-3; chloropyrazine, 14508-49-7; pyrazinetetracarboxylic acid, 43193-60-8; 2,3-pyrazinedicarboxylic acid, 89-01-0; methylpyrazine, 109-08-0; 2,6-dimethylpyrazine, 108-50-9; pyrazinecarboxylic acid, 98-97-5; pyrazine, 290-37-9; 2,5-dimethylpyrazine, 123-32-0; 2,6-dichloropyrazine, 4774-14-5; quinoxaline, 91-19-0; pyrazinecarboxamide, 98-96-4; (4-acetylpyridine)$(NH_3)_5Co^{3+}$, 59389-47-8; (4-benzoylpyridine)$(NH_3)_5Co^{3+}$, 42582-66-1; pyrazine$(NH_3)_5Co^{3+}$, 59389-55-8; fluoro$(NH_3)_5Co^{2+}$, 15392-06-0; chloro$(NH_3)_5Co^{2+}$, 14970-14-0; bromo$(NH_3)_5Co^{2+}$, 14970-15-1; iodo$(NH_3)_5Co^{2+}$, 15392-08-2.

References and Notes

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(13) Note that when the two terms in the denominator of (3) are comparable, the redox reaction is no longer first order in Co(III). Thus when $[PzCONH_2]$ is held at 5×10^{-4} M, increasing the concentration of the chloro complex from 0.001 to 0.004 M accelerates the reaction by a factor of only 2.4 (see the final four chloro entries in Table II). With $[PzCONH_2]$ constant, plots of $1/k_{obsd}$ vs. $[Co^{III}]^{-1}$ should be linear with intercept $1/k_1$. This treatment of our data leads to an extrapolated k_1 value of 0.08 s^{-1}, in reasonable agreement with the value obtained by varying $[PzCONH_2]$.

(14) R. C. Patel and J. F. Endicott, *J. Am. Chem. Soc.*, **90**, 6364 (1968), have reported evidence that $(NH_3)_5CoF^{2+}$ is protonated at high acidities but have not included enough data to evaluate its protonation constant. Such protonation, if it occurs, would make the fluoro group unavailable for bridging and would thus convert a portion of the oxidant to a much less reactive form. For a divergent view, see G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).

(15) In a few instances coordination of 2,2′-bipyridyl to Cr^{2+} has been found to retard its reduction of bound Co(III) slightly. In the large majority of cases, such ligation accelerates reaction, sometimes by several powers of 10. See, for example: A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960); J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(16) Evidence that sulfate and phosphate complexes of Cr(II) react more rapidly than Cr^{2+}(aq) with carboxylate derivatives of $(NH_3)_5Co^{III}$ has been reported by A. Liang, M. Sc. Thesis, Kent State University, 1969, p 26.

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(19) Note that this act of internal electron transfer is symmetry forbidden in the absence of distortion which is unsymmetric with respect to the pyrazine plane. See F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974).

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Electron Transfer. 31. Selectivity in Outer- and Inner-Sphere Reductions of Cobalt(III) by Uranium(III)[1]

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The specific rates of reduction, using U^{3+}, of a variety of organic derivatives of $(NH_3)_5Co^{III}$ are compared to those using other metal reducing centers. log k values for outer-sphere specific rates (25 °C, $\mu = 0.20$) are linearly related to the corresponding log k values for reductions with Cr^{2+}, V^{2+}, Eu^{2+}, and $Ru(NH_3)_6^{2+}$, each with near-unit slope, thus indicating that the Marcus model correlates the action of reductants having standard potentials differing by as much as 0.84 V. For such systems, kinetic selectivity is independent of both reactivity and thermodynamic driving force, in contrast to the situation prevailing for a wide variety of reaction series (featuring partial alteration of covalency in the activation process), for which the most reactive reagents are generally the least selective. Reductions of carboxylatocobalt(III) complexes are inner sphere. Here, again, log k_U values are linearly related to values of log k_{Cr}, log k_{Eu}, and log k_V, as well as to Taft's steric substituent parameters. However, selectivities of the various reducing centers differ, with U^{3+}, by far the *most* reactive, being somewhat more selective than Cr^{2+} and much more selective than Eu^{2+} and V^{2+}. It is suggested that the precursor complex for carboxylato-bridged U^{3+} reductions is analogous to that for Cr^{2+} reductions in that overlap is forbidden between the f_{xz^2} orbital, which holds the third 5f electron of U^{3+}, and the acceptor π orbital of the carboxylato group unless the ligand field of the metal center is unsymmetrically distorted by water molecules in the second coordination sphere, a process adversely affected by large lipophilic groups. For reductions with Eu^{2+}, however, overlap between the f_{z^3} orbital, which accommodates the seventh 4f electron, and the acceptor carboxyl orbital is symmetry permitted, and the susceptibility of reaction rate to the degree of chain branching drops sharply. Results of the present study indicate that, even in the absence of chelation or remote attack centers, selectivity patterns for inner-sphere reductions by f-electron centers are substantially different from those for d-electron centers, due primarily to the different symmetry character of the donor orbitals.

The report, in 1970, by Wang and Espenson[2a] that U^{3+} solutions in aqueous perchlorate media could be prepared and handled without unusual precautions added a powerful and versatile member to the array of reagents conveniently