References and Notes

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Electron Transfer. 41. Rate Enhancement by Ligands in Which Conjugation Is Interrupted[1]

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Seven new carboxylatocobalt(III) complexes, each with a pyridine ring separated from the $-COOCo^{III}$ group by a saturated unit, have been prepared and their reductions with Cr^{2+} and Eu^{2+} studied. Specific rates are well above those for reduction of the ordinary aliphatic and aromatic carboxylato complexes of $(NH_3)_5Co^{III}$ when, and only when, a $-C(=O)NH-$ group lies in the γ position on the ring. Rate enhancement for the Cr^{2+} reduction of complexes of the type $Inic^+-C-COOCo^{III}$ (II and III), in which a single carbon separates the ring and the carboxyl, are particularly striking, exceeding those reported for a number of complexes in which the two functions are in direct conjugation. The rapid europium(II) reductions exhibit strong autocatalytic components, reflecting catalysis of the primary reactions by the ligand released. In these cases, very nearly linear kinetic decay curves demonstrate the specific rate of the uncatalyzed component to be nearly equal to that for Eu^{2+} reduction of the free ligand, which is the initiation step in the catalytic sequence. The properties of the Cr(III) products from the rapid Cr^{2+} reductions correspond to those of a $-COOCr^{III}$ rather than a $-C(NH_2)=OCr^{III}$ complex, indicating coordination of chromium to the carbonyl of the $-COOCo^{III}$ in the activated complexes and ruling out a two-step internal catalytic mechanism. The structures of the very rapid oxidants preclude rate enhancement by chelation or by conjugation of the usual type but appear to allow intervention of a homoallylic type intermediate such as X (or one featuring through-space interaction), in which chromium or europium is bound both to the lead-in carbonyl and, by π interaction, to the activated pyridine ring. It is further suggested that the latter interaction occurs with preliminary, but reversible, electron transfer to the ring. Similar intermediates may intervene in the Eu(II) reductions of the parent ligands, which have been found to be about 10^2 times as rapid as that of the protonated form of isonicotinamide, in which an ^+NH function replaces $^+N-C-COOH$.

Although an array of diverse systems has been described in which inner-sphere reduction of cobalt(III) is strikingly accelerated by bound carboxylato or a related ligand,[2] virtually all such cases fit one of two descriptions. In the first category are substituents in which a donor substituent is available for chelation with the reducing center; these are thought generally to enhance the electron-transfer process by increasing the association constant of the binuclear precursor complex.[3] In quite another group are ligands in which an unsaturated donor function, such as carbonyl or pyridine nitrogen, lies in conjugation with the coordinated carboxyl; these are presumed to increase the rate of internal electron transfer within the precursor.[4,5] Acceleration may be particularly marked when possibilities for both conjugation and chelation exist in the same ligand.[2c,6]

Quite apart from these effects is the catalysis of electron transfer by noncoordinated conjugated species capable of undergoing one-electron reduction to radicals,[7] which, in turn, are known to react very rapidly with cobalt(III) centers.[8] Earlier communications from this laboratory dealt with such catalytic processes.[7b,c,9]

The present study began as an attempt to design an intramolecular analogue of such catalytic systems in which the catalytic center and the oxidizing center are incorporated into a single molecule or ion. It was expected that initial attack on such difunctional oxidants would occur at the catalytic center, followed by rapid electron transfer to Co(III), and that the overall rate of reduction, which would be determined principally by the rate of initiation, might be substantially greater than that for a complex having no such catalytic site. If mechanistic ambiguity were minimized by precluding conjugative interaction between the two centers, such a reaction sequence should constitute a clear-cut example of the radical-ion or chemical mechanism, which has often been proposed[5,10] but infrequently demonstrated[11] for inner-sphere reductions.

We here report our findings concerning the reductions of such insulated bifunctional complexes, including some rate enhancements which are considerably greater than those anticipated. At the same time, however, our evidence suggests that these rapid reductions proceed not through the expected two-step path but rather by a variation of inner-sphere attack at the bound carboxyl.

Experimental Section

Inorganic Materials. Lithium perchlorate,[12] carbonatopentaamminecobalt(III) nitrate,[13] aquopentaamminecobalt(III) perchlorate,[13] and solutions of Cr(II),[13] Eu(II),[14] and V(II)[15] were prepared as described.

Organic Ligands. 4-Carbamoyl-1-(carboxymethyl)pyridinium perchlorate ($Inic^+CH_2COOH(ClO_4^-)$) was prepared by a method similar to that of Craig and co-workers,[16] in which isonicotinamide was alkylated with iodoacetic acid in water. Iodide and unreacted iodoacetate were removed by stirring with three successive portions of anion-exchange resin (Bio-Rad AG 2-X8) in its HCO_3^- form, after

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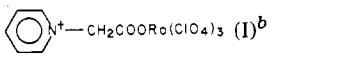
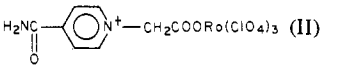
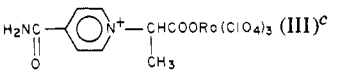
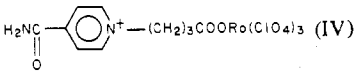
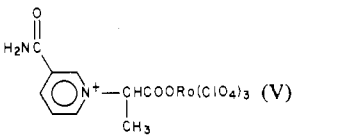
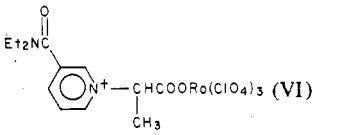
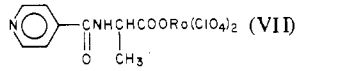
Table I. Analyses of Carboxylatopentaamminecobalt(III) Perchlorates

complex	% C		% H		% Co	
	calcd	found	calcd	found	calcd	found[a]
 (I)[b]	14.50	14.65	3.80	3.90	10.2	9.5
 (II)	15.43	15.46	3.70	3.81	9.5	9.3
 (III)[c]	16.97	16.90	3.93	4.02	9.3	9.1
 (IV)	18.45	18.14	4.15	4.12	9.1	8.4
 (V)	16.97	17.00	3.93	3.98	9.3	8.6
 (VI)	22.53	22.78	4.77	4.96	8.5	8.1
 (VII)	20.15	19.51	4.48	4.82		

[a] Reference 13. [b] "Ro" = roseo = $(NH_3)_5Co^{III}$. [c] % N: 15.17 (calcd 15.41).

which the solution was concentrated to one-third its original volume by rotary evaporation. Addition of 12 M $HClO_4$ then precipitated the ligand as its perchlorate, which was filtered off, washed with cold ethanol and with ether, and then dried in vacuo. 4-Carbamoyl-1-(1-carboxyethyl)pyridinium ($Inic^+CHMeCOOH$) and 3-carbamoyl-1-(1-carboxyethyl)pyridinium ($Nic^+CHMeCOOH$) perchlorates, as well as the *N,N*-diethyl derivative of the latter, were prepared from 2-bromopropionic acid by analogous procedures.

The quaternary butyrato derivative, $Inic^+(CH_2)_3COOH(ClO_4^-)$, was prepared by the procedure of Undheim and Gronneberg,[17] in which equimolar quantities of ethyl 4-bromobutyrate and isonicotinamide in acetonitrile were refluxed for 4 h, after which the solvent was removed by rotary evaporation. The white residue was dissolved in water and treated with $AgClO_4$, the AgBr was filtered off, and the filtrate was made 0.5 M in $HClO_4$. The solution was refluxed for 10 h to hydrolyze the ester, concentrated by rotary evaporation to the onset of crystallization, and then cooled. The white crystalline perchlorate was filtered off and then washed with cold ethanol and with ether.

1-(Carboxymethyl)pyridinium perchlorate ($py^+CH_2COOH(ClO_4^-)$) was prepared from the reaction of ethyl chloroacetate and pyridine without solvent.[18] The ester was hydrolyzed and the acid perchlorate isolated as described above.

DL-Isonicotinylalanine was prepared by the procedure of Gardner and co-workers.[19]

Cobalt Complexes. Carboxylatopentaamminecobalt(III) perchlorates were prepared from the aquopentaammine perchlorate in water,[13] or the carbonatopentaammine perchlorate in diethylene glycol,[12] as described. Contamination with the aquo complex was minimized by chromatography on Bio-Rad Bio-Gel P-2 resin, eluting with water, and then concentrating by rotary evaporation. Contamination with the parent ligands, which are insoluble in water, was minimized by chromatography on Rexyn 102 carboxylic acid resin (Na^+ form), allowing the ligands to pass through as their anionic or zwitterionic forms, and then eluting with dilute $HClO_4$. In troublesome cases, both treatments were necessary. Elemental analyses of these complexes appear in Table I.

Rate Measurements. Rates were estimated from measurements of absorbance changes on the Cary 14 or Beckman Model 5260 recording spectrophotometer or the Durrum–Gibson stopped-flow spectrophotometer as described.[2c,10] Measurements were made at 502 nm. Reactions were first order each in Co(III) and reductant but were generally carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. Most reductions were run in 1.0 M $HClO_4$, but a few were carried out in 0.12 M $HClO_4$ with ionic strength adjusted to near unity with $LiClO_4$. Rates of reduction were independent of $[H^+]$ in the present series. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run agreed to within 5%. Except as noted below, no trends indicating systematic errors were evident, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction times. Specific rates obtained from replicate runs on the Cary or Beckman spectrophotometer checked to better than 8%, whereas successive oxidations on the Durrum (with the same pair of master solutions) were repeated until decay curves for three consecutive runs were superimposable. Specific rates obtained by stopped flow from different master solutions agreed to better than 6%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

The more rapid europium(II) reductions yielded, instead of the usual logarithmic curves, decay curves that were very nearly linear, indicating strong autocatalysis of the type reported in previous studies.[14] These traces were highly reproducible, and reactions exhibiting such behavior were followed essentially to completion. When the fastest reactions in the group were carried out in the presence of a large excess of Eu^{3+}, nearly normal first-order curves, with slight distortion during the later stages of reaction, were obtained.

Stoichiometry Studies. Stoichiometry experiments,[13] in which cobalt(III) and a ligand bound to it were allowed to compete for a deficient quantity of reducing agent, were carried out as described.[6b,13] Results are summarized in Table II. With the slowly reacting 1-(carboxymethyl)pyridinium complex, I, the reaction mixture was allowed to stand for several hours before analyzing for Co(II); the results in this case probably represent a lower limit since reductant almost certainly was partially consumed by traces of oxygen slowly diffusing into the vessel.

Spectra of Products. The visible spectra of the chromium(III) products formed in the very rapid reductions of the 4-$CONH_2$-substituted complexes II and III with Cr^{2+} were taken by adding successive known quantities of reductant to excess Co(III), waiting until spectral changes were no longer detectable, and then subtracting the known absorbancies of the Co(III) complex remaining and Co^{2+} formed. Agreement between spectra calculated at various stages of such "titrations" was good but became poorer beyond the equivalence point as a result of secondary reactions. The spectra from reduction

Table II. Yields of Co(II) (%) from Reduction of Carboxylatopentaamminecobalt(III) Complexes with Cr(II) and Eu(II)[a]

Co(III) complex	Cr(II)	Eu(II)
$py^+CH_2COOCo(NH_3)_5^{3+}$ (I)	39	
$Inic^+CH_2COOCo(NH_3)_5^{3+}$ (II)	98	96
$Inic^+CHMeCOOCo(NH_3)_5^{3+}$ (III)	98	97
py-C(=O)-$NHCHMeCOOCo(NH_3)_5^+$ (VII)	93	86
py-C(=O)-$NHCH_2COOCo(NH_3)_5^{3+}$ (VIII)	90	85

[a] $[H^+] = 1.0$ M; [Co(III)] = 0.01 M; [reductant] = 0.008 M; reductant was added to Co(III).

of the carboxymethyl complex, II, exhibited maxima at 410 (ϵ 22.4) and 575 (20.9) nm, whereas those from reduction of the carboxyethyl derivative, III, showed maxima at 409 (ϵ 23.9) and 576 (23.6) nm. The appearance of isosbestic points at 384, 433, and 561 nm for the carboxymethyl product and at 387, 433, and 561 nm for the carboxyethyl product is evidence against secondary conversions during these reactions (with Co(III) in excess).

Solutions of these Cr(III) products were virtually unaffected by heating in 0.1 M $HClO_4$ at 70 °C for 20 min, but absorbance peaks flattened appreciably (with minimal shift in position) on standing at 90 °C for 30 min. Similar behavior was observed with the Cr(III) products from the known[20] Cr^{2+} reductions of the $(NH_3)_5Co^{III}$ complexes of formic and 2-formylbenzoic acids.

Results and Discussion

Kinetic data are summarized in Table III. All ligands prepared in the present study feature a pyridine ring, and in six of these a carboxamido group is bound to this ring. In no instance does the ring lie in conjugation with the $-COOCo^{III}$ function. Specific rates for reduction with Cr^{2+} (k_{Cr} values) span a range of over 10^4, whereas the scale of k_{Eu} values is somewhat narrower. In each case, reduction of the ring system may, in principle, compete with reduction of Co(III), and the slight, but unmistakable, departures from 1:1 stoichiometry observed in our competition experiments (Table II) reflect this possibility. However, there is no evidence that this competition affects the reliability of our specific rates, which are measured with reductant in large excess.

A major complication is encountered with the fast Eu^{2+} reductions, which yield kinetic traces much more nearly linear than the expected logarithmic decay curves (which are observed with Cr^{2+}). In the extreme case, the Eu^{2+} reduction of the 4-carbamoyl complex, $Inic^+CH_2COOCo^{III}$ (II), yields a trace indistinguishable from a zero-order plot, except during the last few percent of reaction, with no hint of an induction period. Behavior of this type is highly symptomatic of autocatalysis, with the present systems thus closely resembling earlier examples[7a,b,14] in which the catalytic species was identified as the organic ligand liberated in the reduction by Eu^{2+}

$$Lig\text{–}Co^{III} + Eu^{2+} \rightarrow Lig + Co^{II} + Eu^{3+}$$

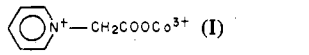
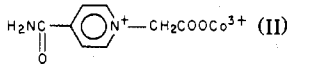
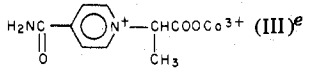
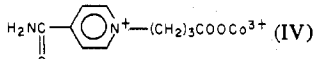
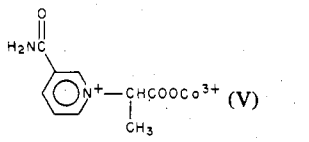
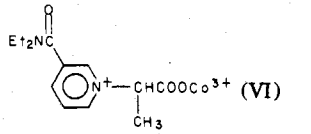
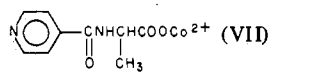
Such ligands have been shown[7a,c,9] to operate through sequence 1 in which "Lig·" is a radical derived from one-electron reduction of the catalyst.

$$Lig \underset{Eu^{3+},\, k_{-1}}{\overset{Eu^{2+},\, k_1}{\rightleftharpoons}} Lig\cdot \xrightarrow[k_2]{Co^{III}} Lig + Co^{2+} \qquad (1)$$

Application of the steady-state approximation to the radical, Lig·, in sequence 1 yields, for a reaction proceeding by a combination of catalyzed and uncatalyzed paths, the rate law given by eq 2 where the k_{Eu} term refers to the uncatalyzed

$$\text{rate} = \frac{k_1k_2[Co^{III}][Eu^{2+}][Lig]}{k_{-1}[Eu^{3+}] + k_2[Co^{III}]} + k_{Eu}[Co^{III}][Eu^{2+}] \qquad (2)$$

Table III. Specific Rates for Chromium(II) and Europium(II) Reductions of Carboxylatopentaamminecobalt(III) Complexes[a]

oxidant	k_{Cr}	k_{Eu}
 (I)	0.039	0.82
 (II)	6.6×10^2 [b]	1.4×10^2 [b,c] 1.6×10^2 [b,d]
 (III)[e]	5.5×10^2 [b]	94[b,c] 97[b,d]
 (IV)	1.9[b]	16[c]
 (V)	0.059	0.45
 (VI)	0.0050[f]	0.30
 (VII)	13.1	2.4
$H_3N^+\text{-}CH_2COOCo^{3+}$	0.064[g]	
$Me_3N^+\text{-}CH_2COOCo^{3+}$	0.016[g]	0.68

[a] Specific rates are in M^{-1} s^{-1} at 25 °C. Reactions were carried out in 1.0 M $HClO_4$ unless otherwise noted. [b] $\mu = 1.2$. [c] Autocatalytic reaction; k_{Eu} is obtained from initial rates. [d] Value obtained from reaction in which autocatalysis was suppressed by addition of 0.08 M Eu^{3+} (see text). Values of k_{Eu} are found to be independent of acidity in the range 0.12–1.20 M H^+. [e] $k_{V(II)}$ for this complex was found to be 1.59 M^{-1} s^{-1} (25 °C, $\mu = 1.0$). [f] $\mu = 0.10$. [g] Reference 23.

reaction. If Eu^{2+} is taken in large excess, $[Co^{III}]_0$ is represented as a, and the extent of overall reaction is represented as x, eq 2 may be rewritten as eq 3. In the systems at hand, k_2 may

$$\text{rate} = \frac{k_1k_2x(a-x)[Eu^{2+}]}{k_{-1}x + k_2(a-x)} + k_{Eu}(a-x)[Eu^{2+}] \qquad (3)$$

be assumed to be substantially greater than k_{-1},[21,22] yielding the simplified expression in eq 4. Thus, the relative mag-

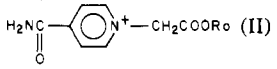
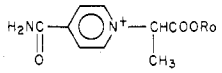
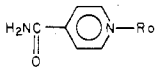
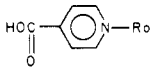
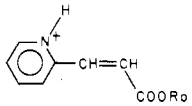
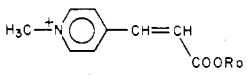
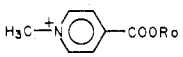
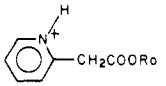
$$\text{rate} = [Eu^{2+}][k_1x + k_{Eu}(a-x)] \qquad (4)$$

nitudes of k_1 and k_{Eu} will determine whether the overall rate will increase or decrease during the course of the reaction. In the present instances, the nearly constant rates imply that these individual k values are nearly equal, that is, that Eu^{2+} transfers an electron to the free ligand as rapidly as to the Co(III)-bound ligand.

As in analogous cases,[7,9] the catalytic path for these Eu^{2+} reactions is inhibited by the addition of excess Eu^{3+}. In the case of the fastest oxidants (II and III), this path is very nearly suppressed for reaction mixtures in which $[Eu^{3+}]/[Co^{III}] > 8$. Values for the uncatalyzed specific rates, evaluated from the first-order curves derived from such mixtures, are seen (Table III) to be in agreement with those taken from initial slopes of linear traces observed in the absence of added Eu^{3+}.

Undoubtedly, the most striking results of the present study are the very high specific rates associated with reductions of the 4-carbamoyl-substituted oxidants II and III. These are the most marked accelerations of this type thus far reported attributable neither to conjugation nor to chelation and, in the Cr^{2+} series, are greater than enhancements observed in a

Table IV. Chromium(II) Reductions of Pyridine-Substituted Carboxylato Derivatives of $(NH_3)_5Co^{III}$

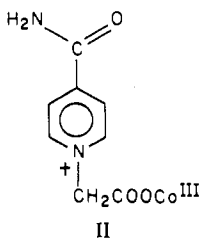
complex	k_{Cr}[a]
 (II)	6.6×10^2 [b]
	5.5×10^2 [b]
	17.4[c]
	10[d]
	3.7[e]
	2.2[e]
	1.4[f]
	0.06[e]

[a] Specific rates in M^{-1} s^{-1} at 25 °C. μ = 1.0 unless otherwise indicated. Ro = "roseo" = $(NH_3)_5Co^{III}$. [b] This work; μ = 1.2. [c] Reference 28. [d] F. R. Nordmeyer, unpublished experiments, University of Rochester, 1970. [e] Reference 2d. [f] Reference 13; μ = 3.0.

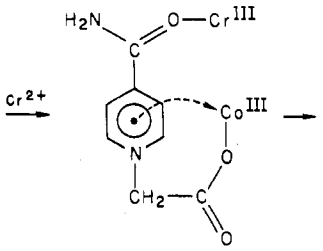
number of systems in which the pyridine ring lies in direct conjugation with $-COOCo^{III}$ (Table IV). The Cr^{2+} rates are particularly remarkable in view of earlier findings[3,23] that attachment of a positive nitrogen near the $-COOCo(NH_3)_5$ center results, in the absence of other effects, in substantial decreases in k_{Cr}.[24] The low rates observed here for the pyridinium complex, I, demonstrate that the observed enhancements do not arise merely from inclusion of the pyridine ring. Incorporation of a carboxamide (or equivalent) function is also necessary, and it is further evident that the latter must be properly situated with respect to the ring nitrogen, for rate enhancement is completely eroded when this substituent is shifted from the γ to the β position (complexes V and VI).

The structural features associated with these rapidly reduced complexes are sufficiently similar to those characteristic of the many electron-transfer catalysts that have been described[7-9] to suggest that the reactions at hand may proceed via internal catalysis, i.e., a two-step sequence in which inner-sphere,[25] one-electron reduction of the pyridine ring precedes electron transfer (through space) to cobalt(III) (eq 5), and that the markedly superior mediating properties here observed for the γ- as compared to the β-substituted ligands reflect the greater ease with which the γ species undergo one-electron reduction.[26,27]

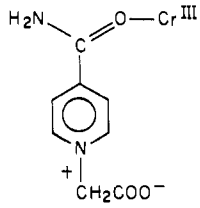
For Cr^{2+} reductions, the sequence shown would lead to an amide-bound chromium(III) product, IX. Species of this type derived from nicotinamide and isonicotinamide have been described by Nordmeyer and Taube,[28] who emphasize the relative ease with which such complexes undergo aquation to the parent amide and $Cr(H_2O)_6^{3+}$. The absorption maxima reported for these amide derivatives (412 and 585 nm) are at lower energies than those observed for the Cr(III) products resulting from the rapid reductions of complexes II and III (409 and 575 nm). More important, our products are much more resistant to aquation. The reported rate constants for aquation of Nordmeyer's amide complexes ($(5-7) \times 10^{-5}$ s^{-1} at 25 °C), in combination with the recorded activation enthalpies, lead to estimated half-life periods of 50 s for aquation at 70 °C, whereas the products from our reactions are unchanged on heating for 20 min at that temperature, although they are found to undergo slow aquation at 90 °C. Thus the properties of the Cr(III) products from oxidants II and III are consistent with carboxyl coordination, but not with amide coordination. Moreover, the appearance of isosbestic points during the rapid electron-transfer reactions constitutes strong evidence against conversion of the primary Cr(III) product to another species on a time scale similar to that of the redox reaction.[29] It is then difficult to avoid the conclusion that the activated complexes in these rapid Cr^{2+} reductions feature coordination of chromium to the carbonyl of the $-COOCo^{III}$ function.[30]



II



VIII



IX

+ Co^{2+} (5)

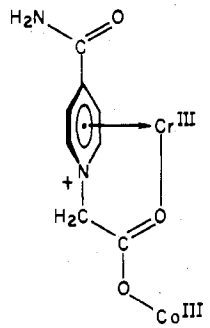
The possibility of a two-step internal-transfer mechanism for the Eu^{2+} reductions of oxidants II and III (which are also rapid) is not so easily dismissed, for the extreme ease of substitution at the Eu(III) center rules out characterization of the primary Eu(III) product. Indeed, the finding that the specific rate for reduction of Co(III), in the absence of external ligand, is very nearly equal to that at which Eu^{2+} transfers an electron to the free ligand to initiate the catalytic sequence would appear to make the internal-transfer mechanism an attractive one in this case, for it may be argued that the rate of electron transfer to the isonicotinamide portion of the ligand should be nearly independent of whether the carboxyl end is free or bound.[28]

There are, however, objections. In virtually all cases where carboxyl lead-in groups are available for electron transfer to Co(III), reductions by Cr^{2+} and Eu^{2+} have been found to follow closely similar patterns.[6b,14b] A more serious point is that electron transfer from Eu^{2+} to the conjugate acid of isonicotinamide, $InicH^+$, has been found[7a,c] to occur at a specific rate of 2 M^{-1} s^{-1} (25 °C, μ = 1.0), i.e., about $^1/_{100}$th of that for electron transfer to $Inic^+CH_2COOH$ and to $Inic^+CH_2COOCo^{III}$. It is difficult to see how substitution of a carboxymethyl group for hydrogen as a side chain can alter the rate so markedly without calling into play an additional reaction path. The mechanism for the rapid Eu^{2+} reductions then remains in doubt, although we favor attack at the carboxyl group, in analogy to the action of Cr^{2+}.

Aside from the possibility of mechanistic variation within the series, the overall question remains as to the source of the rate enhancements which are observed with both reductants. Although earlier studies[7-9] have demonstrated the ease with which the isonicotinamide ring undergoes one-electron reduction, any role assumed by this ring in accelerating net change at the reaction site requires interaction between the two functional units within the ligand, and this interaction

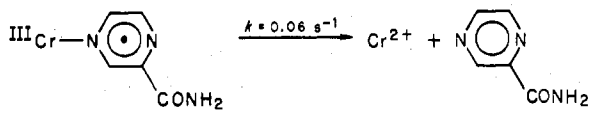
cannot occur by conjugation of the usual type. Interactions between the ring and the carboxyl in the very rapidly reduced $Inic^+$–C–COOCo complexes are, in a formal sense, analogous to homoallylic interactions, for which a large body of evidence now exists, pertaining to both carbonium ion[31] and radical[32] systems. The less markedly accelerated $Inic^+$–C_3–COOCo complex (IV) is likewise analogous to a number of systems in which interaction between functions through space is thought to take place.[33] However, mechanisms for interactions in neither category have as yet been precisely defined, nor is there at present any assurance that a single mechanism accommodates all examples.

Our observations concerning the accelerated reactions appear to be consistent with intervention of intermediates of type X, in which chromium is attached both to the carbonyl



X

group adjacent to ligated Co(III) and, by π bonding, to the pyridine ring. We further suspect that the latter interaction, for which there is little obvious precedent in systems undergoing inner-sphere reactions, occurs with preliminary transfer of an electron to the ring, yielding the Cr(III)–radical complex indicated, and, further, that this transfer, like that between Cr(II) and pyrazinecarboxamide,[34] is reversible. The internal conversion of the Cr(III)-bound radical XI to Cr^{2+}



XI

and the parent ligand has been estimated[34] to proceed at a specific rate of 0.06 s^{-1} at 25 °C, but since isonicotinamide-related radicals are known[9a] to be about 0.40 V more strongly reducing than pyrazine-derived radicals, analogous "back-transfer" in the systems at hand, resulting in reversal of the initial step, may be expected to occur more rapidly than this.[35-41]

Scale models, free of obvious internal strain, may be constructed not only for the proposed intermediate, X, but also for the homologous carboxyethyl and carboxypropyl species (in which a two- and three-carbon chain separates the ring from the carboxyl group) and for presumed analogous intermediates in reductions of the alanine derivative, VII, as well.[42] This extension of the picture is in accord with the observed rate enhancements for oxidants IV and VII (Table III), but we are at present unable to say why the accelerations are greatest when only a single carbon separates the functions.

It is reasonable to suspect the intervention of intermediates similar to X in Eu^{2+} reactions not only with the rapid Co(III) complexes in this series but also with their parent ligands. This is consistent with (although not demanded by) our findings that the reductions of the ligands are much more rapid than that of isonicotinamide itself but proceed at rates nearly the same as those for reductions of the corresponding Co(III) derivatives.[43] To the extent that the proposed picture of the π-coordinated intermediate is realistic, we would expect the formation of such an intermediate to depend principally on the electron affinity of the activated ring and the availability of the carbonyl donor function, and only to a very minor degree on the presence of ligated Co^{III}.

Acknowledgment. The authors are grateful to Professor Francis Nordmeyer for making known his experimental data prior to publication and to Dr. Susan Zawacky and Professors J. E. Gordon, C. F. Hammer, and R. J. Balahura for valuable suggestions concerning preparative procedures.

Registry No. I, 69421-17-6; II, 69421-19-8; III, 69421-21-2; IV, 69421-23-4; V, 69421-25-6; VI, 69421-27-8; VII, 69421-29-0; VIII, 69421-30-3; Cr(II), 22541-79-3; Eu(II), 16910-54-6.

References and Notes

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, is gratefully acknowledged.
(2) See for example: (a) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969); (b) A. Haim, *ibid.*, **8**, 264 (1975); (c) E. S. Gould, *J. Am. Chem. Soc.*, **96**, 2373 (1974); (d) P. K. Thamburaj, M. K. Loar, and E. S. Gould, *Inorg. Chem.*, **16**, 1946 (1977).
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(10) See for example: (a) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965); (b) F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968); (c) H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970); (d) M. M. Itzkowitz and F. Nordmeyer, *ibid.*, **14**, 2124 (1975).
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(21) The ratio of catalytic constants, k_2/k_{-1} (eq 2), for Co(III) complexes featuring the structural sequence $^+$N–C–$COOCo^{III}$ is taken as about 10, the ratio which has been shown[7c] to apply to the Eu^{2+} reduction of $(NH_3)_5Co(py)^{3+}$, as catalyzed by 4-pyridylacrylic acid. To justify this, we assume that carboxylato complexes of the type at hand undergo outer-sphere reduction at rates comparable to that of the benzoylformato derivative of $(NH_3)_5Co^{III}$, which, in turn, has been found[22] to react with $Ru(NH_3)_6^{2+}$ at nearly the same rate as does $(NH_3)_5Co(py)^{3+}$. Note that k_{-1} is independent of the cobalt(III) complex taken.
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(23) R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, **11**, 1965 (1972).
(24) Specific rates for Cr^{2+} reductions of the ordinary aliphatic and aromatic carboxylato complexes of $(NH_3)_5Co^{III}$ cluster in the range 0.1–0.3 M^{-1} s^{-1} (25 °C, μ = 1.0).[2a,13] Rates for carboxylato complexes having a pendent ammonium group lie between 0.004 and 0.06 M^{-1} s^{-1}.[3,23] Values of k_{Eu} appear (at present, unaccountably) to be nearly insensitive to this type of structural modification of the ligand.
(25) Outer-sphere Cr^{2+} reductions of activated pyridine rings have been found[9b] to proceed at specific rates well below 0.1 M^{-1} s^{-1}, much too slowly to accommodate the high k_{Cr} values observed in this study.
(26) The recognized[8,9a,27] greater stabilities of γ-C=O substituted pyridyl radicals is doubtless a conjugative effect. In valence-bond language, structures in which the unpaired electron is situated on the pyridine nitrogen may contribute to the γ radical, but not to the β.

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(29) A very rapid reaction of Cr^{2+} with the primary Cr(III) product, leading to isomerization, must likewise be considered improbable, for it has been noted[26] that reductions, with Cr^{2+}, of $(NH_3)_5Co^{III}$ derivatives are invariably more rapid than the corresponding reactions with $(H_2O)_5Cr^{III}$ derivatives under comparable conditions, although the ratios of specific rates for the two acceptor centers may vary greatly.
(30) The possibility that attack by Cr^{2+} has occurred at a carbanion center at the α position of the chain, generated in response to the acid-strengthening action of the adjacent pyridinium substituent, is inconsistent both with the absence of a $[H^+]$-dependent term in the rate law and with the observed spectra of the Cr(III) products, which are quite unlike those of carbon-bound $(H_2O)_5Cr^{III}$ derivatives (see, for example, M. R. Hyde and J. H. Espenson, *J. Am. Chem. Soc.*, **98**, 4463 (1976)).
(31) See, for example: P. R. Story and B. C. Clark, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. V. R. Schleyer, Eds., Wiley-Interscience, New York, 1972, Chapter 23.
(32) See, for example: J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 466–480.
(33) Examples of interactions through space in carbonium ion systems have been compiled by Story and Clark.[31] For a description of such an effect in a free radical system, see W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976). Further extension to electron-transfer systems has been reported by C. A. Stein and H. Taube, *ibid.*, **100**, 1635 (1978). Such interactions are sometimes described as transannular effects since the groups involved are often incorporated into a ring. Such a description does not properly apply to the interactions in the present study.
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(35) Values of log k for reactions of pyridine-derived radicals with Co(III) centers have been found to be linearly related to the formal potentials of these radicals,[36] with a 0.40-V difference in potential corresponding to about a 10^2-fold acceleration. If it be assumed that a similar relationship holds for reactions with Cr(III) centers, the "back-electron-transfer" in X, resulting in its nonproductive dissociation, may be estimated to proceed at a specific rate near 6 s^{-1}.
(36) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978).
(37) A reviewer reminds us that if the rate of the overall redox reaction is determined by the rate of formation of an intermediate such as X, internal electron transfer to Co(III) must be much more rapid than electron transfer to Cr(III) (which reverses the initial step). It appears that specific rates for internal electron transfer to metal centers within precursor complexes vary over a wide range. Reported values lie in the range 10^{-3}–10^{-2} s^{-1} for Ru(II)–Co(III) systems,[38] approach 10^{-3} for Fe(II)–Co(III) systems,[39] fall between 10^2 and 10^5 for e^-–Co(III) systems,[40] and may be as great as 5×10^5 for some Cr(II)–Co(III) systems.[41] Since the latter two types most closely resemble systems in the present study, it is reasonable to expect electron transfer to Co(III) to compete very favorably with nonproductive dissociation of the precursor in our more rapid systems.
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(42) In the absence of properly substituted pyridine groups, $(NH_3)_5Co^{III}$ complexes of α-acylamino acids are reduced much more slowly. Thus, k_{Cr} has been found to be 0.30 M^{-1} s^{-1} (25 °C, μ = 1.0) for the acetylglycine complex and 0.57 for the benzoylalanine complex. Corresponding k_{Eu} values are 1.99 and 1.96 M^{-1} s^{-1} (C.A.R., unpublished experiments, 1978).
(43) Unpublished experiments by Dr. S. P.-W. Chum (Kent State University, 1978) in which the parent ligand $Inic^+CH_2COOH$ is used to catalyze the Eu^{2+} reduction of $(NH_3)_5Co(py)^{3+}$ yield the specific rate 166 M^{-1} s^{-1} (25 °C, μ = 1.0) for transfer of an electron to the ligand. This value is, as predicted, remarkably close to that for uncatalyzed reduction of the corresponding $(NH_3)_5Co^{III}$ complex (Table III).

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Electron Transfer. 42. Quinoxalinium Radicals[1]

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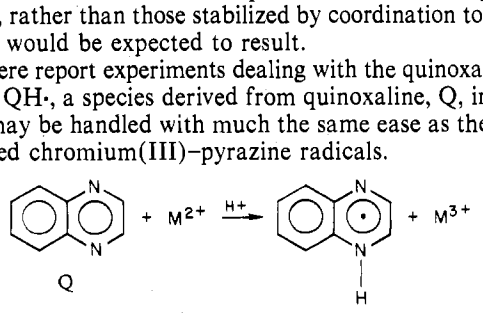
Reduction of quinoxaline with V^{2+}, Eu^{2+}, or Ti^{3+} in 1.2 M $HClO_4$ yields a strongly absorbing yellow species (λ_{max} 357 nm, ϵ 1×10^4), which also exhibits a 15-line ESR spectrum consistent with formulation as the quinoxalinium radical, QH·. Under favorable conditions, this radical persists for over 1 h in aqueous solution. Observed specific rates for the formation of this radical indicate that it is generated by V^{2+} principally via an outer-sphere path but by Eu^{2+} and Ti^{3+} via inner-sphere reductions. Oxidation of the radical by $(NH_3)_5CoBr^{2+}$ proceeds at a rate independent of added quinoxaline, Eu^{3+}, V^{3+}, or Ti(IV), showing that the active species in these reactions is the radical itself, rather than a small quantity of the reducing metal ion in mobile equilibrium with it. The formation of quinoxaline itself, rather than a bromo product, points to an outer-sphere path for this oxidation. It is further found that the quinoxalinium radical does not conform to the linear free-energy relationship which has been found to link the standard potentials of pyridine-related radicals to their outer-sphere reactivities.

The reaction of Cr^{2+} with substituted pyrazines has been shown[1] to yield strongly absorbing chromium(III)-bound radicals, which, in favorable cases, can persist in solution for nearly 1 h. These radical ions reduce one-electron oxidants, and evidence has been presented[2b] that the active intermediate in such reactions is the small quantity of Cr^{2+} in mobile equilibrium with the chromium(III) radical ion. Analogous reductions of pyrazine derivatives with Eu^{2+} and V^{2+} may be envisaged, but since Eu(III) and V(III), in contrast to Cr(III), are labile to substitution in aqueous media, uncomplexed radicals, rather than those stabilized by coordination to metal centers, would be expected to result.

We here report experiments dealing with the quinoxalinium radical, QH·, a species derived from quinoxaline, Q, in acid, which may be handled with much the same ease as the more long-lived chromium(III)–pyrazine radicals.



Q QH·

M = Eu, V

Experimental Section

Materials. Solutions of chromium(II),[3] europium(II),[4] and vanadium(II)[5] were prepared and analyzed as described. Titanium(III) chloride, available in aqueous solution (Matheson Coleman and Bell) was stirred overnight with zinc amalgam to minimize contamination with Ti(IV) and analyzed for Ti(III) by use of the methods of Martin.[6] Substituted pentaamminecobalt(III) perchlorates not available from previous studies[2b,4,7] were prepared by literature procedures.[7,8] Heterocyclic species (Aldrich products) were used as received except for quinoxaline, which was purified by fractional freezing. Water used as solvent was deoxygenated by boiling deionized water for at least 1 h and was then sealed in a flask and purged with deaerated nitrogen for several hours. All reactions were carried out under nitrogen.

Preliminary Observations. The reduced quinoxaline products in this study were generated by mixing solutions of the reducing agent and the quinoxaline derivative, both in 1 M $HClO_4$. Reductions with Eu^{2+}, like the Cr^{2+}–pyrazine reactions described earlier,[2b] were almost immediate with both reagents at the 0.01 M level, whereas reductions with V^{2+} and Ti^{3+} proceeded at measurable rates. The yellow-green Cr^{2+}–quinoxaline product exhibited a maximum at 647 nm (ϵ 230) and a shoulder at 440 nm, but the yellow quinoxaline products with Eu^{2+}, V^{2+}, and Ti^{3+} displayed a single maximum at 357 nm (ϵ 1.0×10^4 in each case). Spectrophotometric titration of quinoxaline with each of the reductants indicated that maximal absorbance occurred at a 1:1 ratio of reactants and that further addition of reductant

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