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$$\Delta G^{\circ'} = \frac{9.10 Z_1 Z_2}{r} \left(\frac{1}{1 + 0.482 r^{1/2}} \right)$$

in which $r = 6.9$ Å, Z_1 and Z_2 are the ionic charges, and l is the ionic strength.

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Electron Transfer. 24. Catalysis of Outer-Sphere Reactions by Noncoordinated Pyridine Derivatives¹

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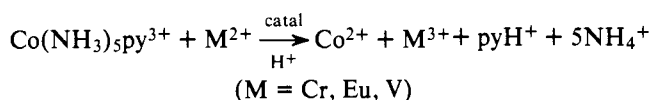
Abstract: The reductions, by Eu²⁺, of a number of Co(III) complexes having no bridging groups are catalyzed by noncoordinated pyridine derivatives having unsaturated substituents γ to the ring nitrogen. Powerful catalysis is observed with 4-pyridinecarboxylic acid (III), its *N*-methyl derivative (I), isonicotinamide (IV), and 4-pyridineacrylic acid (V). Kinetic evidence supports a mechanism in which the catalyst is reduced (k_1) by Eu²⁺ to a radical intermediate, after which this intermediate may react either with Eu³⁺ present (k_{-1}) or with the Co(III) oxidant (k_2). Catalytic effectiveness in these systems is proportional to $k_1 k_2 / k_{-1}$. Measurements under steady-state conditions have given values of k_1 and the ratio k_2 / k_{-1} for ten cobalt(III) oxidants with each of the four catalysts. In addition, earlier pulse radiolytic data⁹ allow estimates of k_{-1} for several of the isonicotinamide catalyzed reactions. The pattern of k_2 / k_{-1} values for the various oxidants is the same for each of the four catalysts and is also similar to the patterns set by the specific rates for reductions by Eu²⁺, V²⁺, Cr²⁺, and Ru(NH₃)₆²⁺ in the absence of catalysis. Log-log plots of k_2 / k_{-1} vs. $k_{\text{uncatalyzed}}$ are linear for the more slowly reacting oxidants, and slopes of the regression lines are near unity with all four catalysts. In this reactivity region, our catalytic systems conform closely to Marcus' model.²³ With the more reactive oxidants, k_2 / k_{-1} ratios approach a maximum value near 15, corresponding to specific rates in the range 10⁶-10⁷ M⁻¹ s⁻¹ for reaction of the radical intermediate with the Co(III) center. For these Co(III)-radical reactions, as for the even more rapid reactions of Co(III) with the nicotinamide radical (XIV) and with the hydrated electron, the multiplicity barrier presumed to be associated with the conversion of low-spin Co(III) to high-spin Co(II) is minimal.

Electron transport processes in living systems commonly involve a plurality of redox species, each of which may exist in either an oxidized or reduced form. The most strongly oxidizing and most strongly reducing members of such groupings rarely react directly, although such action is strongly favored thermodynamically. Instead, an electron is passed successively from one "chain-member" to another which is somewhat more strongly oxidizing and ultimately arrives at the most powerfully oxidizing member of the series.² This mode of action arises, in large part, from the appropriate positioning of such electron transport sites in cell membranes. In effect, the intermediate members of a chain are catalyzing electron transfer between members at either extreme.

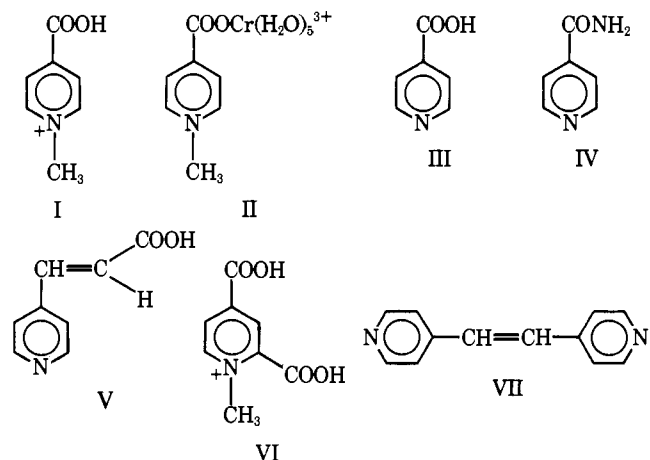
Few situations analogous to this have been described for simple *in vitro* systems involving metal centers. Although there are numerous instances in which added species have been found to accelerate electron transfer between such centers,³ these catalysts generally function either by coordinating with the oxidizing center and acting as a bridge in an inner-sphere process⁴ or by alteration of the character of the reducing agent by prior attachment to it.^{3,5}

In 1971 it was reported⁶ that several pyridinecarboxylate derivatives strongly catalyze the Cr²⁺ and Eu²⁺ reductions of such slowly reacting outer-sphere oxidants as (NH₃)₆Co³⁺ and (NH₃)₅pyCo³⁺. When such catalysts as *N*-methylpyridine-4-carboxylic acid (I) and its (H₂O)₅Cr^{III} complex (II) were employed at the 10⁻⁴ M level at pH 4-5, Cr(II) reductions which, in the absence of catalysis, exhibited half-life periods exceeding 1 h were accelerated into the stop-flow region.^{6a}

Related examples of catalysis of V²⁺ reductions by dicarboxylic acid VI⁷ and of Eu²⁺ and Cr²⁺ reductions by olefin VII⁸ were noted shortly afterwards.

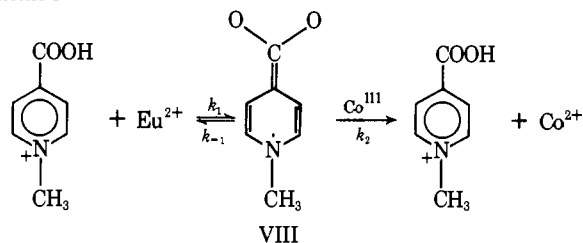


Catalysts:



The structural features common to the catalysts, the chemical nature of the reactants, the kinetic behavior of these catalyzed reactions,⁶ and their inhibition^{6b,7} by Eu³⁺ and V³⁺

Scheme I



point to a catalytic path proceeding through a pyridine-derived radical, formed at small steady-state concentrations, which reacts with the Co(III) oxidant to regenerate the catalyst in its oxidized form. A sequence of the proposed type is shown here as Scheme I. Strong support for such a mechanism is derived from the recent report⁹ that radicals closely related to VIII, generated by pulse radiolysis in the absence of external reductants, rapidly reduce cobalt(III) complexes having no bridging ligands.

The present work deals with reactions of Eu^{2+} ; use of this reductant bypasses complications arising from metal-catalyst coordination (which are encountered in Cr(II)-Cr(III) systems^{6a}) and also avoids difficulties associated with substitution control of reduction rates (which may occur in V(II)-V(III) systems.)^{7,10} The four catalysts chosen, 4-pyridinecarboxylic acid (III), its *N*-methyl derivative (I), isonicotinamide (IV), and 4-pyridineacrylic acid (V), are among the most powerful thus far found for reactions of this type. Our experiments enable us to compare not only the rates at which these are reduced to their respective related radicals, but also the specific rates at which each of the radicals reduces a variety of cobalt(III) oxidants. Despite the magnitude of the latter, their relative values have been found to be closely related to relative values for uncatalyzed reductions by metal centers. The relationship appears to be truncated, however, by the approach to diffusion control with the more rapid oxidants.

Experimental Section

Materials. Cobalt(III) complexes,¹¹ lithium perchlorate,¹² and solutions of $\text{Eu}(\text{ClO}_4)_2$ ¹³ were prepared as described. Except for 4-pyridineacrylic acid (V), which was prepared by the method of Marvel,¹⁴ catalysts were Aldrich products and were used without further purification.

Preliminary Studies. A number of water-soluble aromatic and heterocyclic compounds were examined for catalytic activity, using, as a screening reaction, the reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ (0.002 M) with Eu^{2+} (0.02 M) in 1.2 M or 0.2 M HClO_4 . The reported⁸ specific rate for the uncatalyzed reaction is $0.083 \text{ M}^{-1} \text{ s}^{-1}$. Catalyst candidates were tested initially at the 10^{-3} M level, but if catalytic activity was apparent, experiments at catalyst concentrations as low as 10^{-6} M were carried out. The following compounds were without effect: pyridine, 3-pyridinesulfonic acid, 4-cyanopyridine, 1,2-bis(4-pyridyl)ethane, *p*-aminobenzoic acid, nicotinic acid, 2,6-dimethylpyrazine, aminopyrazine, benzoylformic acid, and di-2-pyridyl ketone. Both 2,5-dimethylpyrazine and *N*-methylpyridine-2-carboxylic acid exhibited slight catalytic activity (a 1.5- to 4-fold increase in rate at the 10^{-3} M level). The following gave strongly absorbing solutions or precipitates which prevented monitoring the desired reaction: 2,6-dichloropyrazine, pyrazinecarboxamide, pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid, phenazine, phenazine methosulfate, and quinoxaline. The following were effective catalysts, but the kinetic picture associated with their action was less straightforward than that for catalysts I-VII: 4-quinolineacrylic acid, *N*-methyl-4-pyridineacrylic acid, quinoline-2-carboxylic acid, 2-phenylquinoline-4-carboxylic acid, and ethyl isonicotinate.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.^{8,11a} Measurements were made at the low-energy maximum of the Co(III) complex (near 475 nm for N-bound oxidants). Reactions were carried out under nitrogen. Transfers of Eu(II) through rubber serum caps were accomplished using hypodermic

syringes. For catalyzed reactions using small quantities of Eu(II), reproducible results were obtained only when transfer syringes were equipped with platinum needles. Reliable rates could not be obtained for uncatalyzed reactions in which Eu(II) was in deficiency. Reactions were first order in Eu^{2+} , very nearly first order in catalyst, and with the reductant in excess, were first order in Co(III). All catalyzed reactions were inhibited by added Eu^{3+} . Rate measurements were made under pseudo-first-order conditions with either Eu^{2+} or Co(III) in greater than fivefold excess. Rates were independent of acidity in the range 0.1–1.2 M H^+ ; most measurements were carried out using 1.2 M HClO_4 as the supporting electrolyte. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 5%. No trends indicative of systematic errors within a single run were noted, and average values did not differ significantly from those obtained from least-squares treatment of 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.

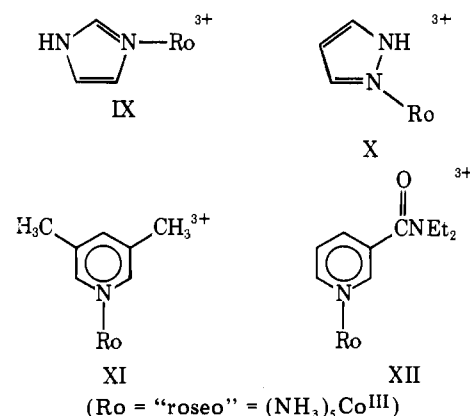
Gradual deterioration of catalyst function with use, as described by Barber,^{6a} could be detected by carrying out a given reduction several times with the same sample of catalyst, but was not troublesome during a single run. The formation of species absorbing in the near ultraviolet and visible regions from the reactions of Eu^{2+} with carboxypyridine derivatives, as reported by Vrachnou-Astra and Katakis,¹⁵ was not observable at the concentrations used in these experiments.

Results and Discussion

Reaction rates are the sum of the catalyzed and uncatalyzed components. The mechanism shown in Scheme I for the catalyzed reaction leads, assuming a steady-state concentration of radical VIII, to the rate law

$$\text{rate} = \frac{k_1 k_2 [\text{Co}^{\text{III}}] [\text{Eu}^{2+}] [\text{catal}]}{k_{-1} [\text{Eu}^{3+}] + k_2 [\text{Co}^{\text{III}}]} + k_{\text{un}} [\text{Co}^{\text{III}}] [\text{Eu}^{2+}] \quad (1)$$

where the k_{un} term refers to the uncatalyzed reaction. This implies a first-order dependence on reductant under all conditions, inhibition by Eu^{3+} (reflecting the reversibility of the initial step in the catalyzed path), and a first-order dependence on Co^{III} when Eu^{2+} is in excess. When the uncatalyzed component is small, reaction should be first-order in catalyst, and if, in addition, Co^{III} is in large excess, rates should become nearly independent both of the concentration of the oxidant and its identity, for electron transfer to the catalyst then becomes rate determining. Each of the oxidant-catalyst systems examined exhibits these kinetic characteristics. With Eu^{2+} in excess, catalytic effectiveness is a composite property and is proportional to $k_1 k_2 / k_{-1}$. Kinetic examination of these systems under steady-state conditions allows evaluation of k_1 and k_2 / k_{-1} , but not all three specific rates. Values of k_{un} have been



(Ro = "roseo" = $(\text{NH}_3)_5\text{Co}^{\text{III}}$)

determined by earlier experiments⁸ on noncatalytic systems.

Ten oxidants are considered in this study. Kinetic data for a typical system, the reduction of $\text{Co}(\text{NH}_3)_5\text{py}^{3+}$ as catalyzed by *N*-methylisonicotinic acid (I), are presented in Table I.

Table I. Kinetic Data for Europium(II) Reduction of Pyridinepentaamminecobalt(III) as Catalyzed by *N*-Methylpyridine-4-carboxylic Acid

[Co ^{III}] × 10 ³	[Eu ²⁺] × 10 ²	[catal] × 10 ⁴	[Eu ³⁺] × 10 ²	<i>k</i> , s ⁻¹ × 10 ² ^a
1.43	2.10	0	0	0.17
1.43	2.10	4.77	2.10	6.0
1.43	2.10	3.18	2.10	3.9
1.43	1.43	4.77	2.10	4.1
1.43	2.14	4.77	2.10	6.3
1.43	2.85	4.77	2.10	7.7
1.43	3.57	4.77	2.10	11.2
1.43	2.10	0.795	2.10	0.96
1.43	2.10	1.59	2.10	1.98
1.43	2.10	3.18	2.10	3.9
1.43	2.10	6.36	2.10	8.2
1.43	2.10	1.59	2.80	1.65
1.43	2.10	1.59	1.40	2.8
1.43	2.10	1.59	0.070	4.5
1.43	2.10	1.59	1.05	3.7 ^b
1.43	2.10	1.59	1.05	3.3 ^c
19.8	0.20	23.1	0	3.9
19.8	0.40	23.1	0	3.8
13.6	0.20	23.1	0	3.9
25.2	0.20	23.1	0	4.1
19.8	0.20	17.4	0	3.3
19.8	0.20	21.3	0	3.9
19.8	0.20	34.7	0	5.8

^a Pseudo-first-order rate constants at 25 °C. Supporting electrolyte was 1.2 M HClO₄ unless otherwise indicated. ^b Reaction mixture was 0.6 M in HClO₄ and 0.6 M in LiClO₄. ^c Reaction mixture was 0.22 M in HClO₄ and 0.98 M in LiClO₄.

When the initial concentrations of Eu²⁺ and Eu³⁺ are much greater than that of Co^{III}, the *k*₂ term in the denominator of eq 1 may be ignored, and plots of the pseudo-first-order rate constants vs. the quotient [Eu²⁺][catal]/[Eu³⁺] are linear with slope *k*₁*k*₂/*k*₋₁. When, on the other hand, *k*₂[Co^{III}] ≫ *k*₋₁[Eu³⁺], plots of rate constants vs. [catal] are linear with slope *k*₁.

Experiments at low Co^{III}, leading to composite rate constants *k*₁*k*₂/*k*₋₁, were carried out with all oxidants, but individual values of *k*₁ could be determined only for those oxidants having a relatively high solubility (greater than 0.02 M) in the perchlorate media used. Composite constants and *k*₁ values are summarized in Tables II and III. As expected, *k*₁, referring to electron transfer to the catalyst, is independent of the Co(III) oxidant taken; moreover, the *k*₁ values obtained here

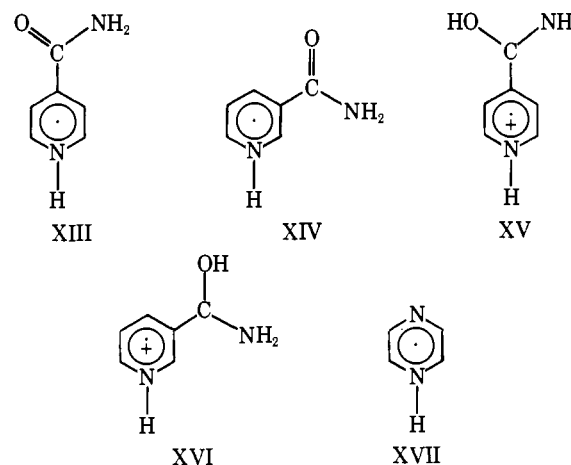
Table II. Europium(II) Reductions of Pentaamminecobalt(III) Complexes, R(NH₃)₅Co^{III}, as Catalyzed by *N*-Methyl-4-pyridinecarboxylic Acid and 4-Pyridinecarboxylic Acid. Composite Rates and Kinetic Parameters

Sixth ligand, R	<i>N</i> -Methyl acid (I)				4-PyCOOH (III)		
	<i>k</i> _{un} ^{a,b}	<i>k</i> ₁ <i>k</i> ₂ / <i>k</i> ₋₁ ^a	<i>k</i> ₁	<i>k</i> ₂ / <i>k</i> ₋₁	<i>k</i> ₁ <i>k</i> ₂ / <i>k</i> ₋₁	<i>k</i> ₁	<i>k</i> ₂ / <i>k</i> ₋₁
Imidazole (IX)	0.0063	13.0	15	0.87	7.7	15	0.50
Pyridine	0.083	115	16	7.1	70	14	5.2
Trimethylacetato	0.163 ^c	10.1	18	0.55	7.9	16	0.48
Pyrazole (X)	0.034	55		3.4	32		2.4
3,5-Lutidine (XI)	0.0022	108		6.7			
<i>N,N</i> -Diethylnicotinamide (XIII)	0.69 ^d	189		12	111		8.1
<i>N,N</i> -Dimethylnicotinamide	0.79 ^d	186		12	180		13
Aquo	0.181 ^d	89		5.6	56		4.1
Co(NH ₃) ₆ ³⁺	0.0017 ^e	6.3		0.39	3.5		0.26
Co(en) ₃ ³⁺	0.00080 ^{d,f}	1.31		0.081	0.87		0.064

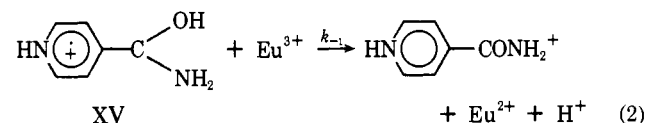
^a Values of *k*_{un} (referring to the uncatalyzed reactions), *k*₁, and the ratio *k*₁*k*₂/*k*₋₁ (see Scheme I) are in M⁻¹ s⁻¹. Temperature 25 °C. Reactions were carried out in 1.2 M HClO₄. ^b Values from ref 8 unless otherwise indicated. ^c Reference 13. ^d This work; $\mu = 1.5$. ^e $\mu = 0.4$; ref 20. ^f See ref 18.

for catalysis by isonicotinamide (IV) are in agreement with that of Norris and Nordmeyer.^{6b} The constancy of *k*₁ allows the ratio *k*₂/*k*₋₁ to be calculated for the less soluble oxidants.

Using pulse radiolysis, Cohen and Meyerstein⁹ have obtained specific rates for the reactions of the isonicotinamide radical XIII, the nicotinamide radical XIV, and the protonated



forms of these radicals (XV and XVI) with several of the oxidants in the present series. Although data for the protonated systems are more limited than for the nonprotonated, their measurements indicate that the nicotinamide radical is about ten times as reactive as the iso radical to each of these Co(III) oxidants, that conversion of XIV to XVI in 1 M HClO₄ lowers its reactivity by a factor of 10 (irrespective of the oxidant), and that the corresponding protonation of the iso radical lowers its reactivity nearly 50-fold. These observations, in conjunction with *k*₂/*k*₋₁ ratios in Table III, allow us to estimate the specific rate with which radical XV reacts with Eu³⁺ (eq 2). Agree-



ment among *k*₋₁ values for three of the systems (Table IV) is seen to be satisfactory, in view especially of the approximate nature of the treatment.

Division of *k*₁ by *k*₋₁ for catalysis by isonicotinamide in strong acid leads to an equilibrium constant 5 × 10⁻⁶ for the reduction of the protonated amide to XV and, taking the potential for the Eu³⁺/Eu²⁺ couple as -0.43 V, to a potential of

Table III. Europium(II) Reductions of Pentaamminecobalt(III) Complexes, $R(NH_3)_5Co^{III}$, as Catalyzed by Isonicotinamide and 4-Pyridineacrylic Acid. Composite Rates and Kinetic Parameters

Sixth ligand, R	Isonicotinamide (IV)			4-Pyridineacrylic acid (V)		
	k_1k_2/k_{-1}^a	k_1^a	k_2/k_{-1}	k_1k_2/k_{-1}	k_1	k_2/k_{-1}
Imidazole (IX)	1.57	2.1	0.75	40	25	1.60
Pyridine	15.4	2.0 ^b	7.6	3.1×10^2	28	11.0
Trimethylacetato	1.26	2.0	0.63	46	28	1.64
Pyrazole (X)	8.4		4.1	2.2×10^2		7.9
3,5-Lutidine (XI)				2.7×10^2		9.6
<i>N,N</i> -Diethylnicotinamide (XII)	17.6		8.8	3.8×10^2		13
<i>N,N</i> -Dimethylnicotinamide	31		16	3.9×10^2		14
Aquo	12.8		6.3	2.1×10^2		7.6
$Co(NH_3)_6^{3+}$	0.88		0.44	21		0.75
$Co(en)_3^{3+}$	0.16		0.078	4.7	28	0.17

^a Values of k_1 and the quotient k_1k_2/k_{-1} (see Scheme I) are in $M^{-1} s^{-1}$. The ratio k_2/k_{-1} is dimensionless. Reaction temperatures were 25 °C. Reactions were carried out in 1.2 M $HClO_4$. ^b This is in satisfactory agreement with the value $1.8 M^{-1} s^{-1}$, reported by Norris and Nordmeyer (ref 6b) for unit ionic strength.

Table IV. Oxidation of the Isonicotinamide Radical Cation, XV, with Europium(III)^a (eq 2)

Competing Co(III) species	k_2^b	k_2/k_{-1}^c	k_{-1}
$Co(NH_3)_5py^{3+}$	3.6×10^6	7.6	4.8×10^5
$Co(NH_3)_5H_2O^{3+}$	3.2×10^6	6.3	5.0×10^5
$Co(NH_3)_6^{3+}$	1.5×10^5	0.44	3.4×10^5

^a Values of k_{-1} and k_2 (see Scheme I) are in $M^{-1} s^{-1}$, 25 °C. ^b From pulse radiolysis data. See ref 9 and text. ^c Ratio for reactions in 1.2 M $HClO_4$ (this work).

−0.74 V for the amide. The latter is in accord with Cohen's value (−0.71 ± 0.06 V),⁹ but diverges substantially from Nordmeyer's earlier estimate (−0.89 V).^{6b}

Comparison of the individual kinetic parameters in Tables II and III emphasizes the manner in which redox catalysis is jointly dependent on the rate at which the catalyst is reduced (k_1) and the competition (expressed as k_2/k_{-1}) between Co(III) and Eu^{3+} for the radical intermediate. Since N-methylation of 4-pyridinecarboxylic acid is seen not to alter its rate of reaction with Eu^{2+} (Table II), the greater catalytic effectiveness of the N-methyl acid merely reflects a more favorable k_2/k_{-1} ratio. In contrast, the advantage enjoyed by 4-pyridineacrylic acid (V) over isonicotinamide (Table III) stems mainly from the greater k_1 value of the acid, although the pattern of k_2/k_{-1} ratios sharpens the trend slightly.

More detailed analysis requires knowledge of the various k_1/k_{-1} ratios, which, in turn, reflect the reduction potentials of the catalysts. Electrochemical measurements on only a few catalyst systems in aqueous perchloric acid have been reported,¹⁶ but it now appears clear that catalytic activity falls off severely if the potential of the catalyst lies outside of the proper range. Thus although radical XIV derived from nicotinamide is known to react very rapidly with bound Co(III),⁹ the parent 3-amide exhibits only marginal catalysis in the systems at hand, since its very high reduction potential (−1.20 V)^{16b} strongly limits the steady-state concentration of the reduced form. On the other hand, pyrazine ($E^\circ = -0.03$ V in 1 M $HClO_4$)^{16a} is reduced virtually completely to the corresponding radical XVII by an equivalent quantity of Eu^{2+} , but this weakly reducing radical reacts more slowly with bound Co(III) than does Eu^{2+} .¹⁷ Hence pyrazine exhibits inhibitory rather than catalytic action in systems of the type considered.

The most striking characteristic of the data in Tables II and

III is that the pattern of k_2/k_{-1} values for the various oxidants is the same for each of the four catalysts. Moreover, if we disregard the trimethylacetato complex, which alone among the oxidants is reduced by Eu^{2+} primarily by an inner-sphere path,¹³ the k_2/k_{-1} patterns are remarkably similar to that for the uncatalyzed specific rates (Table II).

Values of $\log(k_2/k_{-1})$ for each of the catalysts are plotted against $\log k$ for the uncatalyzed reactions in Figure 1.¹⁸⁻²¹ For the more slowly reacting oxidants, the two log functions are linearly related, but k_2/k_{-1} ratios for the more reactive oxidants appear to approach a maximum value near 15 (for all four catalysts). Slopes of the least-squares lines drawn (which include the $Co(NH_3)_5py^{3+}$ complex and the oxidants reacting more slowly than this) are very near unity. Thus, in this region, k_2 is proportional to k_{un} .

Log-log plots having unit slope, although not universal,²² have been reported for outer-sphere redox series involving several pairs of metal-ion reducing centers.^{7,8,13} In such cases, rate differences between the series being compared are much less marked than in the present systems. Here we are dealing with pairs of reductants for which the ratio of specific rates exceeds 10^7 . Despite this very great difference in reactivities, the Marcus model²³ is seen to extend, within the sloping regions of Figure 1, to pyridine-related radicals; i.e., variation in ΔG^\ddagger resulting from alteration of ligation at the Co(III) center are the same for reduction by such radicals as for reduction by Eu^{2+} (and, by implication,¹³ for reduction by $Ru(NH_3)_6^{2+}$, V^{2+} , and Cr^{2+}).

The limits represented by the horizontal lines in Figure 1 correspond to a k_2 near $4 \times 10^6 M^{-1} s^{-1}$ for the isonicotinamide radical⁹ and, in all likelihood, to somewhat higher values for the other radical intermediates.²⁴ Although high, this figure falls below the diffusion-controlled limit near $10^8 M^{-1} s^{-1}$ for bimolecular reactions between +1 and +3 ions of this type in water at 25 °C.^{25,26} It is perhaps reasonable to attribute this modest gap to the multiplicity barrier,²⁷ which is presumed ordinarily to be associated with the conversion of low-spin Co^{III} (t_{2g}^6) to Co^{II} ($t_{2g}^5 e_g^2$). However, the studies of Farina and Wilkins²⁸ indicate that this barrier becomes minimal for reactions having sufficiently negative values for ΔG ; moreover, Cohen and Meyerstein⁹ find that radical XVI derived from the protonated form of nicotinamide reduces $(NH_3)_5Copy^{3+}$ and $(NH_3)_5CoH_2O^{3+}$ at specific rates very near $10^8 M s^{-1}$. We therefore suspect that the limiting specific rates for reduction by radical XV reflect superposition, onto the diffusion-controlled limit, of a small activation barrier associated with the distortion of this radical in conjunction with the act of electron transfer, but we cannot explain (even in a tentative fashion)

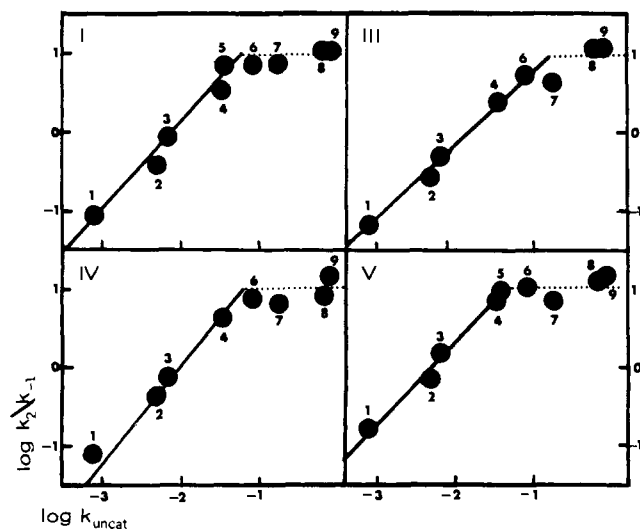


Figure 1. Log-log plot comparing ratios k_2/k_{-1} (see Scheme I in text) for catalyzed reductions of Co(III) complexes by Eu^{2+} , with the specific rates for the corresponding uncatalyzed reductions (k_{uncat}). Catalyzed reactions were carried out in 1.2 M HClO_4 at 25 °C; rate constants for uncatalyzed reactions have been adjusted to $\mu = 1.2$. Individual oxidants are: (1) $\text{Co}(\text{en})_3^{3+}$, (2) $\text{Co}(\text{NH}_3)_6^{3+}$, (3) $\text{Ro}(\text{imidazole})^{3+}$, (4) $\text{Ro}(\text{pyrazole})^{3+}$, (5) $\text{Ro}(3,5\text{-lutidine})^{3+}$, (6) Ropy^{3+} , (7) $\text{Ro}(\text{H}_2\text{O})^{3+}$, (8) $\text{Ro}(N,N\text{-diethylnicotinamide})^{3+}$, and (9) $\text{Ro}(N,N\text{-dimethylnicotinamide})^{3+}$ ($\text{Ro} = \text{"roseo"} = (\text{NH}_3)_5\text{Co}^{\text{III}}$). Slopes of the diagonal least-squares lines to the left of the break points are for the indicated catalysts: I (*N*-methylpyridine-4-carboxylic acid) 1.05; III (pyridine-4-carboxylic acid) 0.97; IV (isonicotinamide) 1.10; V (4-pyridineacrylic acid) 1.03.

why this barrier for the isonicotinamide radical is greater than that for its 3-isomer, XVI.

In sum, we have presented evidence that each of the four redox catalysts taken is reduced by Eu^{2+} , incompletely and at a moderate specific rate, to a pyridine-related radical, that these radicals react rapidly both with Eu^{3+} and bound Co(III), that the kinetic reaction patterns with the less reactive Co(III) complexes closely follow the patterns observed for uncatalyzed reductions by a variety of metal center reducing agents, and that specific rates for the more reactive Co(III) complexes approach a maximum near, but not equal to, the diffusion-controlled limit.

References and Notes

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- (18) The specific rate here observed for the uncatalyzed $\text{Co}(\text{en})_3^{3+}\text{-Eu}^{2+}$ reaction ($0.00080 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 1.5$) is not in agreement with the earlier approximate value, $0.005 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 1.0$.¹⁹ Note that the latter value exceeds the more recently recorded specific rate for the $\text{Co}(\text{NH}_3)_6^{3+}\text{-Eu}^{2+}$ reaction under similar conditions,²⁰ whereas in each of the other instances where these two oxidants have been reduced by a given metal center, the hexaammine has been found to react substantially more rapidly.^{3,21}
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