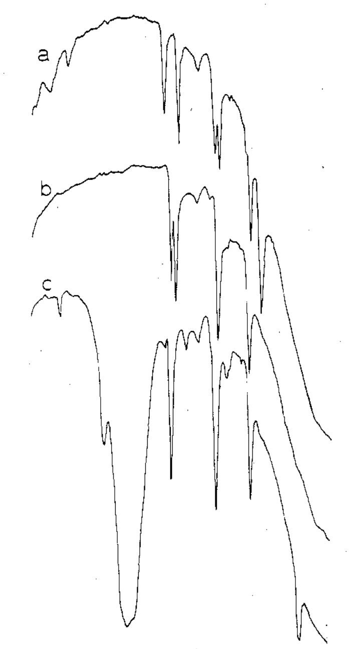

Figure 2. Nujol mull infrared spectra of $[(py)_2Br]ClO_4$ (a), $[(py)_2Br]Br_3$ (b), and $[(py)_2Br]PF_6$ (c). Note the splittings in the bands at 690 and 766 cm^{-1} in b and c, indicative of nonequivalent pyridines.

large difference in σ values for the 3,5-dibromopyridine–bromine complex from the halogen data and the value of σ determined from the ^{14}N NQR data for the pyridine adduct suggests that there may be a difference in the structures. The relatively small degree of charge transfer from the base to Br_2 in the 3,5-dibromopyridine compound suggests that the compound may be molecular rather than ionic in character. On the other hand, 3,5-dibromopyridine should be a substantially weaker Lewis base than pyridine itself. In any case both the IR[10] and ^{14}N NQR data suggest that the pyridine adduct is best formulated as the $[(py)_2Br]Br_3$ salt.

In the bis(pyridine)bromine(I) hexafluorophosphate salt, the bonding of the pyridines is equivalent, while for the Br_3^- salt there is a nonequivalence of the pyridines as determined by the ^{14}N NQR data. The nonequivalence is even larger in the case of the ClO_4^- salt. This trend is confirmed in the IR spectra shown in Figure 2, in which a splitting of the 766 and 690 cm^{-1} pyridine C–C out-of-plane bending vibrations is seen in the spectrum of the Br_3^- salt; an even larger splitting is evident in the spectrum of the ClO_4^- salt. The loss of centrosymmetry in the cation in these salts may be caused by packing effects in which the anion resides above the more positive pyridine ring of the cation. A similar effect is not noted in the $(py)_2I^+$ salts.

If we assume an ionic structure for $py{\cdot}Cl_2$, the acidities of the halogen cations, as reflected in the σ values for the coordinated pyridine, are in the order $I^+ < Br^+ < Cl^+$. The fact that the σ for the chlorine compound, 1.22, is substantially less than the values for the bromine(I) and iodine(I) compounds (around 1.59, and 1.62, respectively) is further argument that structure III is the correct structure for the chlorine compound.

Registry No. $py{\cdot}Cl_2$, 40007-00-9; $py{\cdot}BrCl$, 21300-57-2; $py{\cdot}ICN$, 15802-02-5; $py{\cdot}ICl$, 6443-90-9; $py{\cdot}IBr$, 6443-62-5; $py{\cdot}I_2$, 2078-94-6; $[(py)_2Br]PF_6$, 21584-58-7; $[(py)_2Br]Br_3$, 21682-18-8; $[(py)_2Br]ClO_4$, 53514-32-2; $[(py)_2I]I_7$, 72174-99-3; $[(py)_2I]ClO_4$, 15699-62-4.

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Electron Transfer. 44. Decreases in the Effectiveness of Redox Catalysts with Use[1]

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Received April 17, 1979

Pyridine derivatives, which, when uncoordinated, catalyze outer-sphere electron-transfer reactions between metal centers, often undergo loss of catalytic activity with use. The active intermediates in such catalyzed reactions are radicals (cat·) formed by initial reaction of the catalysts with the primary reducing centers. This study examines the deterioration of a number of such catalysts in reactions of Eu^{2+} and V^{2+} with $(NH_3)_5Co(py)^{3+}$. This deterioration, when it occurs, arises from interaction of the catalyst and the reducing center; it does not require Co(III). Degrees of deterioration vary widely. The very powerful catalysts derived from 2,4-pyridinedicarboxylic acid (III) lose much or all of their catalytic activity during the course of a single 1-min run with Eu^{2+} in excess, whereas catalytic erosion of isonicotinic acid (I), its esters, and its nitrile is negligible after treatment with excess reductant for 10–20 min. Erosion is much more marked with Eu^{2+} than with the less strongly reducing V^{2+} and is much less severe when the oxidant, rather than the reductant, is taken in excess. Deterioration in Eu^{2+} systems may be decreased strikingly by addition of excess Eu^{3+} and that in V^{2+} systems by addition of V^{3+}. The spectra of the products formed when the more fragile catalysts react rapidly with Eu^{2+} (in the absence of Co(III)) correspond to those formed by reduction of the catalysts with zinc amalgam, which is presumed to be a two-electron reductant. The more robust isonicotinate catalysts are not affected by Eu^{2+} under similar conditions. Evidence is presented in support of two attrition mechanisms. The catalytic deterioration of 2,4-pyridinedicarboxylic acid in Eu^{2+} systems appears to involve disproportionation of catalyst–radical pairs ($2cat{\cdot} + 2H^+ \rightarrow cat + catH_2$), converting one member of each pair to an inactive dihydro species and returning the other to the catalyst pool. Measurements of the rate of deterioration of this catalyst allow us to estimate the specific rate for the disproportionation as $5.8 \times 10^8\ M^{-1}\ s^{-1}$. In systems featuring less fragile catalysts (e.g., isonicotinamide) the steady-state concentration of the radical, cat·, is so low that attrition, if it takes place at all, occurs mainly by reductive deterioration ($cat{\cdot} + Eu^{2+} \xrightarrow{2H^+} Eu^{3+} + catH_2$). In two such instances, comparison of kinetic runs using catalyst preparations that have undergone partial attrition permits an estimate of the specific rates of such deteriorative processes. Although both modes of attrition are presumed to occur in each catalytic system, bimolecular disproportionation appears to compete most favorably with reductive deterioration when the extent of reduction of the catalyst to its radical is greatest.

Previous communications dealing with the catalysis of electron-transfer reactions between metal centers by uncoordinated aromatic species contributed evidence that such catalysis proceeds by preliminary reduction of the aromatic to

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a free radical, which then reacts rapidly with the oxidizing center.[2] It was emphasized, both in the early reports[2b] and in descriptions of more detailed studies,[2c-e] that such catalysts undergo deterioration with use, an effect which is sometimes evident during a single catalytic run. The extent of this erosion depends not only on the catalyst and reagents taken but also on reaction conditions and the order in which the reagents are mixed.[2d,e] With Cr^{2+} as a reductant, this deterioration may be attributed, in large part, to coordination by the substitution-inert Cr(III) center to the catalyst molecule,[2b,d] blocking off possible lead-in groups of the latter, but this cannot be the case for reductions by Eu^{2+}, V^{2+}, and U^{3+}, for ligand substitutions about the resulting metal centers, Eu(III), V(III), and U(IV), are known to be rapid.[2e]

The results of the present investigation, which deals specifically with loss of catalytic effectiveness in some Eu(II)–Co(III) and V(II)–Co(III) systems, support the view that this attrition is due principally to conversion of the aromatic radical intermediates, via a combination of disproportionation and "overreduction" to catalytically inactive two-electron reduction products. We also present data on some new catalytic species, several of which have been found to be more resistant to attrition than those previously described.

Experimental Section

Materials. Solutions of europium(II)[3] and vanadium(II)[4] were prepared by published procedures. (Pyridine)pentaamminecobalt(III) perchlorate, $Co(NH_3)_5py(ClO_4)_3$, the primary oxidant in the catalytic runs, was prepared as described.[5] Of the catalysts used, the 2-monomethyl ester and the diester of 2,4-pyridinedicarboxylic acid were prepared by the method of Thunus,[6] the N-methylated 2,4-diacid by the procedure of Meyer,[7] and 4-carbamoyl-1-(carboxymethyl)-pyridinium perchlorate $[(Inic^+–CH_2COOH)(ClO_4^-)]$ by the method of Craig and co-workers.[8] Isonicotinic esters of ethylene glycol and glycerol were prepared as described by Badgett and Woodward[9] and were converted to their hydroperchlorates by treatment with aqueous 3 M $HClO_4$. Poly(vinyl isonicotinate) was prepared from isonicotinyl chloride[9b] and poly(vinyl alcohol) (average mol wt 2000) as described by Pizzirani and Magagnini.[9c] 2,4,6-Pyridinetricarboxylic acid was prepared by the method of Tropsch.[9d] Other catalysts (Aldrich products) were used as received.

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at the low-energy Co(III) maximum, 475 nm, using a Cary 14 or Beckman 5260 recording spectrophotometer as described.[2c,3b] Reactions were generally carried out in 1.0 M $HClO_4$. Measurements were made under pseudo-first-order conditions with either Co(III) or the reductant in greater than fivefold excess. To evaluate catalyst deterioration, which was shown to occur only when the catalyst and the reductant were present together, we used two procedures. With the reductant in excess, reductant, catalyst, and supporting electrolyte were mixed, and after a measured time interval, the oxidant was added. The resulting kinetic curve was then compared to one from a mixture in which there were no delay in adding Co(III). With Co(III) in excess, oxidant, catalyst, and supporting electrolyte were premixed, and successive "shots" of the reductant were added at measured intervals great enough to allow the reaction resulting from each shot to proceed to >98% completion.[10] Reactions were first order in Eu^{2+}, were very nearly first order in catalyst, and with reductant in excess (and Eu^{3+} or V^{3+} added) were first order in Co(III). Reactions were followed for at least 5 half-lives. For reactions involving the most robust catalytic systems, constants evaluated from successive half-life values within a single run generally agreed to within 6%, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance difference against reaction time. Specific rates obtained from replicate runs, each with fresh catalyst, agreed to within 8%. When catalyst deterioration within a run was perceptible but slight, half-life periods were extrapolated to zero time, and the resulting limiting value was used to calculate the specific rate. Kinetic traces resulting from reductions catalyzed by 2,4-pyridinedicarboxylic acid with Eu^{2+} in excess did not approximate simple first-order curves but corresponded to a superposition, onto the primary reaction, of a second-order decay of the catalyst.[11] Reactions catalyzed by poly(vinyl isonicotinate) did not give tractable kinetic curves. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Table I. Typical Kinetic Data for the Europium(II) Reduction of (Pyridine)pentaamminecobalt(III) As Catalyzed by Ethylene Glycol Diisonicotinate

$10^3[Co^{III}]$	$10^3[Eu^{2+}]$	$10^2[Eu^{3+}]$	$10^4[cat]$	10^2k,[a] s^{-1}
1.11	25.8	0	0	0.20
1.11	25.8	2.58	1.81	4.5
1.11	25.8	2.58	0.91	2.2
0.37	25.8	2.58	0.91	2.3
1.11	25.8	5.16	1.81	2.5
1.11	25.8	1.72	1.81	5.3
1.11	25.8	2.58	2.72	6.3
1.11	17.2	2.58	1.81	2.9
1.11	34.4	2.58	1.81	5.3
1.11	43.0	2.58	1.81	6.3
5.40	0.49	0	3.62	1.00
5.40	0.98	0	3.62	0.94
5.40	0.49	0	1.81	0.49
3.08	0.49	0	3.62	0.92
5.40	0.49	0	5.43	1.39

[a] Pseudo-first-order rate constants at 25 °C. Reactions were carried out in 1.0 M $HClO_4$.

Reduction of the Catalysts. Spectrophotometric studies of the reductions of several of the catalysts by Eu^{2+} were carried out in the region 220–400 nm by treating 0.003 M solutions of the catalysts in 1.0 M $HClO_4$ with 50-fold excess of Eu^{2+} under N_2, waiting 3 min, bubbling air through the solution for about 30 min[12] to oxidize excess Eu^{2+} (which exhibits absorption maxima at 262 and 320 nm[13]), diluting eightfold with 1.0 M $HClO_4$, and then recording the spectrum. An

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(1) Sponsorship of this work by the National Science Foundation (Grant CHE 77-14950) is gratefully acknowledged.

(2) See, for example: (a) C. Norris and F. Nordmeyer, *J. Am. Chem. Soc.*, **93**, 4044 (1971); (b) J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971); (c) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *ibid.*, **99**, 1073 (1977); (d) Y.-T. Fanchiang, J. C.-K Heh, and E. S. Gould, *Inorg. Chem.*, **17**, 1142 (1978); (e) M. K. Loar, Y.-T. Fanchiang, and E. S. Gould, *ibid.*, **17**, 3689 (1978).

(3) (a) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974); (b) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).

(4) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(5) E. S. Gould, N. A. Johnson, and R. B. Morland, *Inorg. Chem.*, **15**, 1929 (1976).

(6) L. Thunus and M. Dejardin-Duchene, *J. Pharm. Belg.*, **24**, 3 (1969).

(7) (a) H. Meyer, *Monatsh. Chem.*, **24**, 199 (1903); (b) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(8) (a) J. H. Craig, P. C. Huang, T. G. Scott, and N. J. Leonard, *J. Am. Chem. Soc.*, **94**, 5872 (1972); (b) C. A. Radlowski and E. S. Gould, *Inorg. Chem.*, **18**, 1294 (1979).

(9) (a) C. O. Badgett and C. F. Woodward, *J. Am. Chem. Soc.*, **69**, 2907 (1947); (b) H. Meyer and R. Graf, *Ber. Dtsch. Chem. Ges.*, **61**, 2202 (1928); (c) C. Pizzirani and P. L. Magagnini, *J. Appl. Polym. Sci.*, **11**, 1173 (1967); (d) H. Tropsch, *Monatsh. Chem.*, **35**, 777 (1914).

(10) The second of these procedures, involving recycling, is, in principle, applicable also to systems in which the reductant is in excess. Such recycling experiments were found to yield deterioration values close to those obtained by premixing and waiting. Precision was less satisfactory, however, for it was found that despite normal precautions, dilute Eu(II) solutions in rubber-capped cells may slowly lose reducing power (with catalyst absent) each time the cap is punctured and the solution agitated. Related difficulties have been described by J. Doyle and A. G. Sykes, *J. Chem. Soc. A*, 2936 (1968).

(11) The integrated rate equation corresponding to this situation is $\log[Co^{III}]_0 - \log[Co^{III}] = (k_1/k_D[cat]_0)\log(1 + k_Dt[cat]_0)$ where k_1 is the pseudo-first-order rate constant for the redox reaction being monitored and k_D that for decay of the catalyst to an unreactive species. With $[Eu^{2+}] = 0.0233$ M, $[Eu^{3+}] = 0.0467$ M, $[cat]_0 = 5.6 \times 10^{-6}$ M, and $[Co^{III}]_0 = 0.002\,30$ M, for example, the observed kinetic curve follows this relationship with $k_1 = 0.13\ s^{-1}$ and $k_D = 3.7 \times 10^4\ M^{-1}\ s^{-1}$.

(12) It was shown that the spectra of the reduction products derived from the γ-substituted catalysts used were not significantly altered by aeration or on standing several hours at room temperature. This stability contrasts with the behavior reported for a number of β-substituted pyridine reduction products. [See, for example, S. G. A. Alivastos, F. Ungar, and G. J. Abraham, *Biochemistry*, **4**, 2616 (1965).]

(13) M. Faraggi and Y. Tendler, *J. Chem. Phys.*, **56**, 3297 (1972).

Table II. Catalyzed Europium(II) Reductions of (Pyridine)pentaamminecobalt(III): Composite Rates and Kinetic Parameters

catalyst	k_1k_2/k_{-1}[a]	k_1	k_2/k_{-1}
isonicotinamide[b]	15.4	2.0	7.6
ethyl isonicotinate	54	6.2	8.7
ethylene glycol diisonicotinate (II)	2.1×10^2	25	8.2
glyceryl triisonicotinate	3.4×10^2	40[c]	
4-cyanopyridine	7.7×10^2	23	33[e]
4-carbamoyl-1-(carboxymethyl)pyridine (V)	6.8×10^2	170	4.1
2-carboxy-4-(carbomethoxy)pyridine	6.6×10^3	6×10^2 [d]	

[a] Values of k_1 and the quotient k_1k_2/k_{-1} (see sequence 1) are in M^{-1} s^{-1}. The ratio k_2/k_{-1} is dimensionless. Reactions were carried out in 1.0 M $HClO_4$ at 25 °C. [b] Reaction medium 1.2 M $HClO_4$ (see ref 2c). [c] Estimated value, taking k_2/k_{-1} as 8. [d] Estimated value, taking k_2/k_{-1} as 10 (see ref 2d). [e] Because of the relatively high k_2/k_{-1} ratio associated with this catalyst, kinetic runs with Eu^{2+} in excess, from which k_1k_2/k_{-1} is derived, yield reasonable pseudo-first-order curves only if the ratio $[Eu^{3+}]/[Co^{III}]$ taken exceeds 40.

analogous procedure was used to study the solutions resulting from reductions of the catalysts with zinc amalgam, except that the reaction period was increased to about 2 h and the air oxidation was omitted. Spectra from the Zn–Hg reductions could be examined to wavelengths as low as 200 nm since there was no interference from Eu^{3+}, which absorbs strongly between 200 and 220 nm.

Results and Discussion

In accord with earlier studies,[2] the catalytic mechanism in these reactions is taken to be sequence 1, which leads, on application of the steady-state approximation to the intermediate, "cat·", to rate law 2. The final term, involving k_{un},

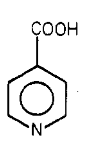
$$\text{cat} \underset{M^{3+},\, k_{-1}}{\overset{M^{2+},\, k_1}{\rightleftharpoons}} \text{cat}\cdot \xrightarrow[k_2]{Co^{III}} \text{cat} + Co^{2+} \qquad (1)$$

$$M = Eu, V$$

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

pertains to the uncatalyzed reaction. The latter is nearly negligible for those Eu^{2+} reductions carried out with fresh catalytic samples but must be taken into account for all reductions by V^{2+} and for those Eu^{2+} reductions in which the catalytic path has been eroded. As before, apparent kinetic behavior reflects the competition between M^{3+} and Co(III) for cat·, the radical intermediate. With Co(III) in deficiency and M^{3+} added, the k_{-1} term in the denominator of the catalytic fraction is dominant, and the reaction appears to be first order in Co(III) and inhibited by M^{3+}, whereas with Co(III) in excess, the catalyzed rate becomes nearly independent of oxidant.

Typical kinetic data, pertaining to the reduction of $Co(NH_3)_5py^{3+}$ by Eu^{2+}, as catalyzed by ethylene glycol diisonicotinate, II, are given in Table I. With Co(III) in excess, plots of pseudo-first-order rate constants vs. [cat] give k_1 (as slope). With Co(III) in deficiency, plots of rate constants vs. $[cat][Eu^{2+}]/Eu^{3+}]$, which are closely linear, yield, as slopes, the quotient k_1k_2/k_{-1}. The resulting parameters for catalysts examined quantitatively for the first time are summarized in Table II. For those cases where k_1 has not been obtained directly, it may be approximated by dividing k_1k_2/k_{-1} by an estimated value of k_2/k_{-1}, for the latter is known to vary only slightly for a series of structurally related catalysts operating in a given redox system.[2d,14-16] Steady-state experiments alone will not yield individual values of k_{-1} and k_2.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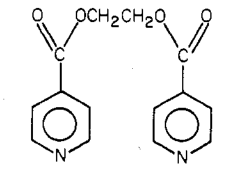
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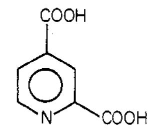
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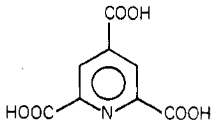
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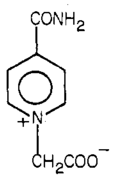
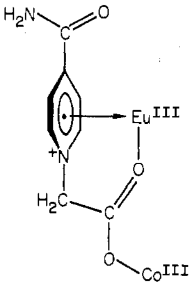

V

The high k_1 values bolster earlier evidence[14a] that electron transfer from Eu^{2+} to catalysts of this type (and, by implication, the oxidation of the resulting radicals by Eu^{3+}) are inner-sphere processes.[17] Of particular interest are the parameters for 4-cyanopyridine, the first catalytically active nitrile to be reported,[18] and for the *N*-(carboxymethyl) derivative, V. Note that in the latter catalyst substitution of a CH_2COOH group for the ring-bound proton in the acid form of nicotinamide has increased the rate of initial attack by a factor of 85. Indeed, the k_1 value for V lies remarkably close to the specific rate (170 M^{-1} s^{-1})[8b] at which the $(NH_3)_5Co^{III}$ complex of the same acid is reduced (at the Co^{III} center) by Eu^{2+}. Evidence has been presented[8b] that this Co^{III}–Eu^{2+} reaction proceeds through an intermediate of type VI, in which the reducing center interacts with both the carboxyl group and the pyridine ring, and we suspect the intervention of a similar intermediate in the one-electron reduction of the uncoordinated acid.


VI

Data in Table III illustrate the diminution of catalytic action in reductions by Eu^{2+}, and Table IV summarizes the results of a similar, but more limited, study of V^{2+} reductions. The extent to which the various catalysts deteriorate in the presence of reductant is seen to vary widely. The very powerful[4d] catalysts derived from 2,4-pyridinedicarboxylic acid (III) lose virtually all their catalytic activity after 1 min (approximately the duration of a single kinetic run). The *N*-(carboxymethyl) derivative, V, is only slightly more robust, whereas apparent loss of reactivity in the reactions catalyzed by isonicotinic acid, its esters, and its nitrile under similar conditions is marginal and due probably to slight loss, on long standing, of reducing

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(14) (a) Y.-T Fanchiang, J. C. Thomas, V. D. Neff, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **16**, 1942 (1977); (b) Y.-T. Fanchiang and E. S. Gould, *ibid.*, **16**, 2516 (1977).

(15) In the limiting case, when both k_{-1} and k_2 pertain to outer-sphere processes, the ratio k_2/k_{-1} is, as predicted by Marcus,[16] very nearly independent of the catalyst taken.[14b]

(16) (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(17) Catalytically active pyridine derivatives which are devoid of lead-in donor functions have been found to react with Eu^{2+} at specific rates near 0.5 M^{-1} s^{-1} (25 °C, μ = 1.0).[14b]

(18) L. H.-C. Hua, R. J. Balahura, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, **17**, 3692 (1978).

Table III. Deterioration of Catalytic Action in the Europium(II) Reduction of (Pyridine)pentaamminecobalt(III)

catalyst	$10^3[\mathrm{Co^{III}}]$, M	$10^2[\mathrm{Eu^{2+}}]$, M	$10^2[\mathrm{Eu^{3+}}]$, M	10^4[cat], M	delay, min	10^2k,[a] $\mathrm{s^{-1}}$	activity retained,[b] %
isonicotinic acid (I)	2.30	2.35	2.35	5.62	0	4.8	
					5.0	4.4	91
N-methylisonicotinic acid	2.30	2.35	2.35	1.62	0	2.5	
					29	2.3	91
ethyl isonicotinate	2.30	2.35	2.35	2.78	0	1.90	
					20	1.85	97
4-cyanopyridine	2.33	2.35	9.07	3.23	0	5.1	
					20	4.8	94
isonicotinamide	2.30	2.33	2.33	8.13	0	1.08	
					10	0.78	67
	2.30	2.33	4.67	8.13	0	0.76	
					10	0.60	72
	2.30	2.33	9.34	8.13	0	0.52	
					10.5	0.46	82
	2.30	2.33	2.33	6.67	0	0.80	
					25	0.51	52
					55	0.37	30
4-carbamoyl-1-(carboxymethyl)pyridine (V)	2.31	2.33	2.33	0.51	0	5.6	
					1.0	0.67	9
					4.0	0.48	6
	2.31	2.33	13.9	0.51	0	1.60	
					1.0	1.27	72
	5.4	0.049	0	2.4	0	3.5	
					5.0	3.3	95
					10	3.2	97
ethylene glycol diisonicotinate (II)	1.46	2.13	2.13	1.21	0	3.5	
					5.0	3.4	97
	5.4	0.049	0	3.62	0	1.00	
					10	0.97	97
glyceryl triisonicotinate	1.46	2.13	2.13	0.898	0	3.0	
					5.0	2.9	98
2,4-pyridinedicarboxylic acid (III)	2.30	2.33	4.67	0.056	0	12.5[c]	
					1.0	0.18	<2
	2.30	2.33	14.6	0.028	0	2.0	
					1.0	0.69	28
2,4,6-pyridinetricarboxylic acid (IV)	30.1	0.33	0	0.13	0	>5	
					1.0	0.16	<2[d]
N-methyl-2,4-pyridinedicarboxylic acid	1.23	2.28	2.28	0.059	0	2.7[e]	
					5.0	0.17	<3
2-carboxy-4-(carbomethoxy)pyridine	1.20	2.13	2.13	0.041	0	2.1[e]	
					5.0	0.17	<3

[a] Pseudo-first-order rate constants at 25 °C. Reactions were carried out in 1.0 M $\mathrm{HClO_4}$. [b] In calculation of the percent catalytic activity remaining, corrections were applied for the uncatalyzed component ($k = 0.083\ \mathrm{M^{-1}\ s^{-1}}$).[3b] [c] Initial specific rate. Analyses of kinetic curves indicate that the primary redox reaction was accompanied by a decay of active catalyst proceeding at a second-order specific rate $3.7 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ (see Experimental Section and footnote 11). [d] With $\mathrm{Eu^{2+}}$, rather than $\mathrm{Co^{III}}$, in excess, decay of catalyst was so rapid that only a small portion of the catalytic component could be detected. [e] Extrapolated value. Apparent specific rate decreased perceptibly during the course of the reaction (see Experimental Section).

Table IV. Deterioration of Catalytic Action in the Vanadium(II) Reduction of (Pyridine)pentaamminecobalt(III)

catalyst	$10^3[\mathrm{Co^{III}}]$, M	$10^2[\mathrm{V^{2+}}]$, M	$10^2[\mathrm{V^{3+}}]$, M	10^3[cat], M	delay, min	10^2k,[a] $\mathrm{s^{-1}}$	activity retained,[b] %
4-carbamoyl-1-(carboxymethyl)pyridine (V)	1.98	2.04	4.08	1.74	0	1.23	
					1.0	0.96	64
					5.0	0.86	51
2,4-pyridinedicarboxylic acid (III)	2.11	2.04	4.08	0.94	0	4.2	
					5.0	3.7	86
					60	2.6	57
N-methyl-2,4-pyridinedicarboxylic acid	2.11	2.04	2.04	0.328	0	2.6[c]	
					15	1.10	29
	2.11	2.04	4.08	0.328	0	1.77[c]	
					5.0	1.22	57
					15	0.96	41
	2.11	2.04	8.16	0.328	0	1.38	
					15	1.03	62
dimethyl 2,4-pyridinedicarboxylate	1.32	2.02	2.02	0.098	0	2.89	
					5.0	2.17	70

[a] Pseudo-first-order rate constants at 25 °C. Reactions were carried out in 1.0 M $\mathrm{HClO_4}$. [b] In the calculation of the percent catalytic activity remaining, corrections were made for the uncatalyzed component. [c] Extrapolated value. Apparent specific rate decreased perceptibly during the course of a run (see Experimental Section).

agent by reaction with traces of oxygen. Comparison of Tables III and IV shows the decreases in catalytic activity to be much more severe with $\mathrm{Eu^{2+}}$ than with the less strongly reducing center, $\mathrm{V^{2+}}$. Note that marked loss of activity does not require the presence of Co(III);[10] indeed, deterioration may be minimized by adding sufficient Co(III), for it is seen to become much less severe when oxidant, rather than reductant, is taken in excess.

Two mechanisms for catalytic deterioration may be considered: (1) conversion of the catalyst radical, through further action of the reducing center, to a less active or a catalytically inactive dihydro species or (2) consumption of the catalyst by bimolecular destruction of the radical intermediate, i.e., by dimerization or disproportionation. The first of these, reductive deterioration, implies a competition between Co^{III} and the reductant M^{2+} for the active intermediate, cat·, and would therefore be expected to become less pronounced when the ratio $[M^{2+}]/[Co^{III}]$ is decreased or when Eu^{2+} is replaced by the more sluggish[14a,20] reductant, V^{2+}. The second possible mode, bimolecular destruction, increases in importance as the steady-state concentration of the intermediate, cat·, which is given by expression 3, rises. Hence, erosion by this route also

$$[\mathrm{cat}\cdot] = \frac{k_1 k_2 [M^{2+}][\mathrm{cat}]}{k_{-1}[M^{3+}] + k_2[\mathrm{Co^{III}}]} \tag{3}$$

may be minimized by decreasing the ratio of reductant to oxidant or by substitution of V^{2+} for Eu^{2+} (which would decrease k_1 but increase k_{-1}[14a]), and the same should hold true if a combination of the two types of process is involved.

For Eu^{2+} reduction, as catalyzed by the fragile catalyst 2,4-pyridinedicarboxylic acid (Table III), erosion appears to be, in substantial part, bimolecular, for the catalyst is seen to decay, by a second-order process, during the course of a single run. Moreover, the catalytic behavior of the closely related and very fragile catalyst 2,4,6-pyridinetricarboxylic acid, IV, allows us to choose between disproportionation of the radical intermediate and its dimerization as the chief mode of termination. Dimerization of the radical from this catalyst may be presumed to involve bonding between two pyridine rings. The new bond in this instance would be flanked by four ortho carboxyl groups, and its formation should then be subject to some steric retardation. Since, however, this catalyst is found to undergo deterioration *more rapidly* than any other in the present series, we may infer that its radical is being lost by disproportionation, rather than by dimerization. Extension of this conclusion to other radical intermediates derived from the most fragile catalysts is reasonable, in view especially of recent evidence of Kosower and co-workers[21] that 4-substituted pyridinyl radicals closely related to ours undergo disproportionation much more rapidly than dimerization in acidic media.

Representing the disproportionation as eq 4 implies that each

$$2\mathrm{cat}\cdot \xrightarrow{2H^+} \mathrm{cat} + \mathrm{catH_2} \tag{4}$$

act converts one of two radicals to a catalytically inactive dihydro species, $catH_2$, and returns the other to the pool of active catalyst molecules. If so, the rate of deterioration, on the molecular level, is just half that of radical disproportionation, although in the attrition process a sample of catalyst may in time be nearly completely converted to a dihydro product or a mixture of such products.

In the case of some of the more robust catalyst systems, for which attrition is too slow to be observed during a single run, our experiments indicate, however, that loss of catalyst occurs mainly through reductive deterioration, i.e.

$$\mathrm{cat}\cdot + \mathrm{Eu^{2+}} \xrightarrow[k_{\mathrm{rd}}]{2H^+} \mathrm{Eu^{3+}} + \mathrm{catH_2} \tag{5}$$

Assume, for long standing times, that diminution in reactivity results from a combination of catalyst deterioration and, to a lesser extent, loss of reductant by adventitious processes not involving the catalyst. If the steady-state approximation is again applied to the radical cat·, the relative rate at which activity is lost, $(-dk_{\mathrm{obsd}}/dt)/k_{\mathrm{obsd}}$, can be shown to be

$$\frac{-dk_{\mathrm{obsd}}/dt}{k_{\mathrm{obsd}}} = \frac{k_1 k_{\mathrm{rd}}[\mathrm{Eu^{2+}}]^2}{k_{-1}[\mathrm{Eu^{3+}}] + k_{\mathrm{rd}}[\mathrm{Eu^{2+}}]} + C \tag{6}$$

where k_{obsd} is the pseudo-first-order rate constant observed with Co^{III} in deficiency, k_{rd} the specific rate for reduction of the radical to $catH_2$, and C the catalyst-independent loss of reactivity on standing. If the k_{rd} term in the denominator is assumed to be much smaller than the k_{-1} term, the deterioration equation should feature a term inverse first order in Eu^{3+} (or in V^{3+}), leading, in turn, to the integrated form (7) in which

$$\ln\,(k^0_{\mathrm{obsd}}/k^t_{\mathrm{obsd}}) = \left[\frac{k_1 k_{\mathrm{rd}}[\mathrm{Eu^{2+}}]^2}{k_{-1}[\mathrm{Eu^{3+}}]} + C\right]t \tag{7}$$

k^0_{obsd} is the observed pseudo-first-order rate constant with fresh catalyst and k^t_{obsd} is that with a catalyst which has been allowed to deteriorate for time t. In contrast, deterioration by reaction of two alkyl radicals should lead to an attrition term proportional to $[Eu^{3+}]^{-2}$.

For the Eu^{2+} reductions catalyzed by isonicotinamide (Table III) with $[Eu^{2+}] = 0.0233$ M, $[\mathrm{cat}] = 8.13 \times 10^{-4}$ M, and a deterioration period of 10 min, the ln k function in (7) has been found to be linearly related to $[Eu^{3+}]$ added:

$$\ln\,(k^0_{\mathrm{obsd}}/k^t_{\mathrm{obsd}}) = \frac{0.0067}{[\mathrm{Eu^{3+}}]} + 0.15 \quad (t = 600\ \mathrm{s}) \tag{8}$$

which is of the same algebraic form as (7), thus pointing to reductive deterioration as the principal mode of attrition. Similarly, the V^{2+} reductions catalyzed by *N*-methyl-2,4-pyridinedicarboxylic acid (Table IV), with $[V^{2+}] = 0.0204$ M, $[\mathrm{cat}] = 3.28 \times 10^{-4}$ M, and a waiting period of 15 min, conform to an analogous relationship:

$$\ln\,(k^0_{\mathrm{obsd}}/k^t_{\mathrm{obsd}}) = \frac{0.0197}{[\mathrm{V^{3+}}]} + 0.35 \quad (t = 900\ \mathrm{s}) \tag{9}$$

leading to the same conclusion in this system. Note further that both attrition mechanisms, bimolecular termination and reductive deterioration, lead ultimately to the same unreactive product, the dihydro derivative, $catH_2$.

Our picture derives further support from spectral comparisons (Table V) of catalyst preparations which have been treated with excess Eu^{2+} to those reduced with zinc amalgam, which may be considered to operate as a two-electron donor. The observed 10–20-nm shifts of the low-energy maxima may be taken as characteristic of two-electron reductions of 4-substituted pyridines of this kind to dihydro derivatives. The predominant absorbing species from each catalyst appear to be the same for the two reductants although complications from secondary reactions may occur in individual cases. Note the difficulty with which isonicotinic acid and its esters are reduced by Eu^{2+}. No changes in these catalysts are detected 3 min after mixing, a reaction period in which conversion of the derivatives of 2,4-pyridinedicarboxylic acid and the *N*-(carboxymethyl) catalyst, V, appears to be nearly complete, and even after over 60 min, Eu^{2+} reductions of the isonicotinate catalysts are only partial. The resistance exhibited by catalysts in the latter group is in accord with the persistence of their catalytic activity under conditions where isonicotinamide and the very powerfully catalytic dicarboxylato derivatives in this series undergo partial or complete deterioration.

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(19) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5593 (1973).

(20) It is here assumed that reduction of the intermediate "cat·" to a two-electron product is, like the initial one-electron reduction of the added catalyst, an inner-sphere process.[14a]

(21) E. M. Kosower, A. Teuerstein, H. D. Burrows, and A. J. Swallow, *J. Am. Chem. Soc.*, **100**, 5185 (1978).

Table V. Spectra of Catalyst Preparations before and after Reduction

	λ_{max}, nm (ϵ^a)		
catalyst	before redn	reduced with Eu^{2+} [b]	reduced with Zn–Hg
isonicotinamide	262 (4.9)	252 (4.9)	252 (4.7)
	213 (4.0)	257 sh	257 sh
			215 (4.7)
4-carbamoyl-1-(carboxymethyl)pyridine (V)	266 (6.6)	257 (5.5)	255 (5.2)
	223 (9.0)	263 sh	262 sh
		222 (8.7)	224 (9.6)
isonicotinic acid (I)	272 (4.7)[c]		
	210 sh		
ethyl isonicotinate[d]	272 (5.6)	260 (2.9)	
	216 (10.2)		
4-cyanopyridine[e]	280 (5.0)	275 (2.0)	
	275 (1.6)	259 (3.6)	
	227 sh		
glyceryl triisonicotinate[d]	274 (7.6)	273 sh	
	215 (12.1)	255 (7.9)	253 (8.2)
		216 sh	218 (7.4)
2,4-pyridinedicarboxylic acid (III)	279 (6.6)	266 (2.2)	262 (1.9)
		273 sh	
dimethyl 2,4-pyridine dicarboxylate	278 (7.0)	266 (2.7)	266 (0.8)[e]
	286 sh	273 sh	273 sh
2,4,6-pyridinetricarboxylic acid (IV)	291 (3.3)	*f*	
	284 (3.8)		

[a] ϵ values in $M^{-1}\ cm^{-1} \times 10^{-3}$; solvent 1.0 M $HClO_4$. For reaction conditions, see Experimental Section. [b] Spectra of the Eu^{2+} reduction products in the range 200–215 nm could not be obtained because of strong absorbance by Eu^{3+}. [c] No change in spectrum on treatment with Eu^{2+} for 60 min. [d] Spectrum of catalyst exhibited virtually no change on treatment with Eu^{2+} for 3 min. Spectra given for Eu(II)-reduced preparations were obtained after 1–4 h, at which time vestiges of peaks from the unreduced catalysts were still apparent. [e] In contrast to results with Eu^{2+} alone, no change in spectrum was observed on treatment with a 4:1 Eu^{3+}:Eu^{2+} ratio (in simulation of conditions used in the kinetic runs, Table III) for 51 min. [f] Spectrum became essentially featureless in the range 220–400 nm after 3-min treatment with Eu^{2+}.

If the present interpretation is correct, the very nearly (over 95%) complete reduction of isonicotinamide (see eq 10), at

$$2Eu^{2+} + cat + 2H^+ \rightarrow 2Eu^{3+} + catH_2 \qquad (10)$$

the 0.003 M level, with 0.15 M Eu^{2+} in 1 M $HClO_4$, when considered together with the standard potential −0.379 V reported for the Eu^{2+}/Eu^{3+} couple in aqueous perchlorate,[22] implies a formal potential less negative than −0.42 V for the two-electron reduction (designated $E°_{02}$) for this catalyst. This lower limit lies well above −0.66 V, the potential for one-electron reduction (the $E°_{01}$ value) for isonicotinamide in 1 M $HClO_4$,[23] and we may in turn set a lower limit of −0.18 V for the potential of reduction of the radical intermediate, $E°_{12}$ ($=2E°_{02} - E°_{01}$). Thermodynamically, then, the radical from isonicotinamide is a stronger oxidant than its parent species by at least 0.48 V.[24]

The specific rate, k_t, for the bimolecular destruction of the radical intermediate in a more rapidly deteriorating catalytic system may be estimated from the extent of deterioration in a single run. In the reaction catalyzed by 2,4-pyridinedicarboxylic acid, with $[Eu^{2+}] = 0.0233$ M and $[Eu^{3+}] = 0.0467$ M, catalytic decay is seen[11] to occur at a rate corresponding to $3.7 \times 10^4[cat]^2$. Assuming disproportionation to be the sole decay mode allows us to set this rate equal to $k_t[cat\cdot]^2/2$. The ratio $[cat\cdot]/[cat]$ under these conditions may be estimated[25] to be 0.010, leading to a value $5.8 \times 10^8\ M^{-1}\ s^{-1}$ for k_t.[26] This bimolecular rate constant, which falls slightly below the diffusion-controlled limit for reactions in water at 25 °C, is very similar to decay constants reported for a number of 4-substituted pyridinyl[21] and related[27] radicals in aqueous systems.

In instances where attrition occurs principally by reductive deterioration, we may use the $[Eu^{3+}]^{-1}$ term (or the $[V^{3+}]^{-1}$ term) in the deterioration equation, (8) (or (9)), to estimate k_{rd}, the specific rate at which the radical cat· suffers destructive reduction. For the Eu^{2+}–isonicotinamide system, the known[23] potential of the catalyst in 1 M $HClO_4$ implies a k_1/k_{-1} ratio of 1.8×10^{-5}, which, in conjunction with fixed values of $[Eu^{2+}]$ (0.0233 M) and t (600 s), leads to a value of $1.1 \times 10^3\ M^{-1}\ s^{-1}$ for k_{rd}. Analogous treatment[28] of attrition data for V^{2+} reductions as catalyzed by *N*-methyl-2,4-pyridinedicarboxylic acid (Table IV) yields $k_{rd} = 2.3 \times 10^3\ M^{-1}\ s^{-1}$.

Although quantitative deterioration studies have been carried out on only a few systems, it appears that attrition through bimolecular disproportionation becomes most important when the extent of reduction of the catalyst to its radical is greatest, i.e., when we are dealing with a readily (1e) reducible catalyst and a reducing center having a highly negative potential. In cases where conversion to a radical is less, reductive deterioration (which is only unimolecular in [cat·]) may compare more favorably with disproportionation.

In sum, catalytic deterioration in electron-transfer systems may be minimized by (a) lowering the fraction of catalyst converted to the radical intermediate at steady state and (b) decreasing the specific rate of bimolecular disproportionation, that of reductive deterioration, or both. With a given catalyst, the extent of radical conversion may be reduced, as seen, by working in a medium having a less negative potential, i.e., by addition of excess oxidant or the oxidized form of the reducing center. Alternatively, one may select a catalyst with a more strongly negative potential, but in so choosing, one sacrifices initial catalytic potency, for it has been shown[23] that the ratio k_1k_2/k_{-1} for pyridine derivatives, which is a measure of catalytic effectiveness under the unusual conditions, decreases steadily as $E°_{cat}$ falls. As for deceleration of termination, it is apparent from earlier studies[21,27] that closely related heterocyclic radicals may undergo destruction at substantially different specific rates. Athough the structural factors governing such rates have not been pinpointed, we suspect that disproportionation (which, in the cases at hand, involves

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(23) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978).

(24) Note that spontaneity of disproportionation of a radical intermediate of this type requires that $E°_{12}$ be less negative than $E°_{01}$ but does not set limits on the difference[12] between the two potentials.

(25) The pseudo-first-order specific rate ($0.125\ s^{-1}$, Table III) noted for the Eu^{2+} reduction of $(NH_3)_5Co(py)^{3+}$, as catalyzed by 2,4-pyridinedicarboxylic acid at the reagent levels specified, corresponds[2c] to a k_1k_2/k_{-1} ratio of $4.5 \times 10^4\ M^{-1}\ s^{-1}$ for this system. This value, in conjunction with a relationship which has been found[23] to link such catalytic ratios with the formal potentials of the catalyst and the reducing center, allows us to estimate the potential of this diacid as −0.475 V. The latter, along with the Eu^{3+} potential −0.379 V,[22] leads to an equilibrium constant 2.3×10^{-2} for the reaction $Eu^{2+} + cat \rightarrow Eu^{3+} + cat\cdot$ and, in turn, to a $[cat\cdot]/[cat]$ ratio of 0.0105.

(26) If dimerization, as well as disproportionation, contributes to catalyst destruction, the estimated k_t value will be too large. Correction for this effect can be made by dividing by $(1 + f_d)$, where f_d is the fraction of terminations resulting from dimerization.

(27) See, for example, E. Hayon and M. Simic, *J. Am. Chem. Soc.*, **95**, 1029 (1973).

(28) The pseudo-first-order specific rate (Table IV) for the V^{2+} reduction, as catalyzed by *N*-methyl-2,4-pyridinedicarboxylic acid, after correction for the uncatalyzed kinetic component, gives[2c,25] a k_1k_2/k_{-1} ratio of 65 $M^{-1}\ s^{-1}$, which, in combination with the reported[14b] reduction potential of V^{3+} (−0.242 V) in this medium, allows us to estimate[23] $E°$ for this catalyst as −0.518 V and k_1/k_{-1} for this system as 2.2×10^{-5}. The latter ratio, in conjunction with the coefficient of the $[V^{3+}]^{-1}$ term in (9) and the fixed values of $[V^{2+}]$ and t, leads to $k_{rd} = 2.3 \times 10^3\ M\ s^{-1}$.

electron rather than atom transfer) can be retarded by reducing the accessibility of the π orbitals which accommodate the unpaired electron and that this might be accomplished by attachment of bulky substituents on the ring or by incorporating this ring into a larger structure of limited flexibility. Whether such structural modifications might selectively minimize destructive radical–radical interactions without proportionately retarding the desired reactions of the catalyst with the primary reaction centers remains to be seen.

The present study also points to significant differences in the ease with which the several catalyst radicals undergo further reduction. Those isonicotinate catalysts which, in our hands, exhibit essentially no deterioration have potentials very close to that of isonicotinamide[14a] and thus yield about the same concentrations of their radicals under comparable catalytic conditions. Their longevity in use must therefore be attributed to lower k_{rd} values, the specific rate for reductive deterioration (eq 5). Since the latter reaction requires two protons, it may be that this difference reflects, at least in part, the difficulty with which the esters and nitrile undergo diprotonation in comparison to the more basic amide. Further pursuit of this point is desirable.

Acknowledgment. The authors are indebted to a reviewer for fundamental and valuable suggestions regarding interpretation of kinetic data in this study.

Registry No. I, 55-22-1; II, 72121-34-7; III, 499-80-9; IV, 536-20-9; V, 72121-35-8; isonicotinamide, 1453-82-3; ethyl isonicotinate, 1570-45-2; glyceryl triisonicotinate, 72121-36-9; 4-cyanopyridine, 100-48-1; 2-carboxy-4-(carbomethoxy)pyridine, 24195-03-7; *N*-methylisonicotinic acid, 824-77-1; *N*-methyl-2,4-pyridinedicarboxylic acid, 62778-02-3; dimethyl 2,4-pyridinedicarboxylate, 881-86-7; $(NH_3)_5Co(py)^{3+}$, 31011-67-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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Electron-Transfer Reactions of Copper(I) and Copper(III) Complexes

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Received July 20, 1979

The reactions of bis(2,9-dimethyl-1,10-phenanthroline)copper(I), $Cu^I(dmp)_2^+$, and of bis(2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate)cuprate(I), $Cu^I(dpmp)_2^{3-}$, with copper(III)–oligopeptide complexes are quite rapid with rate constants varying from 2×10^4 M^{-1} s^{-1} to 2.5×10^8 M^{-1} s^{-1}, indicating that outer-sphere electron transfer occurs. The cross exchange rate constants, k_{12}, for the reactions $Cu^{III}(peptide) + Cu^IL_2 \xrightarrow{k_{12}} Cu^{II}(peptide) + Cu^{II}L_2$, where L is dmp or $dpmp^{2-}$, are determined for a series of copper(III) peptides, where the $E°_{12}$ values vary from −0.11 to +0.32 V. The values of k_{12} for the reduction of copper(III) by $Cu^I(dmp)_2^+$ exhibit a correlation with $E°_{12}$ consistent with the Marcus theory. This is not the case for the reductions with $Cu^I(dpmp)_2^{3-}$, which have unusual behavior in two regards. First, the observed first-order rate constants reach limiting values as the concentration of excess reductant increases, but limiting values are not observed if Cu(III) is used in excess. Second, the k_{12} rate constants (obtained under conditions where the rate depends on both the Cu(III) and the Cu(I) concentrations) approach a limiting value of 10^6 M^{-1} s^{-1} and are independent of $E°_{12}$. Neither anomalous behavior is observed for the $Cu^I(dmp)_2^+$ reactions with Cu(III) complexes.

Introduction

The study of the aqueous chemistry of the copper(I) ion is severely limited by the disproportionation equilibrium[1] eq 1.

$$2Cu^I \rightleftarrows Cu^{II} + Cu^0 \qquad (1)$$

Metastable solutions of aquocopper(I) can be prepared only in highly acidic media.[2] The redox kinetics of this ion with iron(III),[3] vanadium(IV),[4] cobalt(III)[5], and mercury(II)[6] appear to follow inner-sphere mechanisms.

A number of ligands form strong complexes with the copper(I) ion[7] and may be used to prevent disproportionation. Among the better characterized of these copper(I) complexes are derivatives of 1,10-phenanthroline (phen). Several spectroscopic[8,9] and thermodynamic[10,11] studies have been reported. More recently,[12,13] the kinetics of redox reactions involving these complexes have been studied and there appears to be serious disagreement in the calculated self-exchange rate constants for $Cu^{II,I}(phen)_2^{2+,+}$ evaluated from different cross reactions. Holwerda and co-workers[12] report a value of 5×10^7 M^{-1} s^{-1} while Yandell[13] reports a value of 68 M^{-1} s^{-1}. Yandell also reports values of 1.7×10^4 and 4.4×10^4 M^{-1} s^{-1} for the $Cu^{II,I}(dmp)_2^{2+,+}$ self-exchange rate constant evaluated from studies of the reduction of $Cu^{II}(dmp)_2^{2+}$ by cytochrome *c* and $Co^{II}(phen)_3^{2+}$, respectively.[13]

Oligopeptide complexes of copper(III) have been prepared and UV-visible[14,15] and circular dichroism[16] spectroscopic properties and potentiometric behavior[15] have been investigated. Spectroscopic and kinetic properties of copper(III)–peptide complexes strongly suggest that they are square planar with structures typified by that of the triglycinamide complex (structure I). The reduction potentials of the copper(III)–oligopeptide complexes are sensitive to the nature of the lig-

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