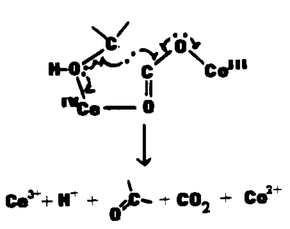
Scheme I



Co(III) center, and less than half has been found to be converted to Co^{2+} (Table III).

If it is assumed that electron transfer from the hydroxyl group to Ce(IV) occurs by an inner-sphere path, the lactato, mandelato, and benzilato reactions should proceed through intermediates having compositions and structures corresponding to the Ce(IV)-Co(III) complexes detected spectrophotometrically (Table II). It further appears that the breakage of the C-C bond and the electron transfer to Co(III) are concerted, for without the former there is no reasonable mode by which the effects of alteration at the Ce(IV)-O site may be transmitted to Co(III). Moreover, our experiments give no hint that other species intervene between formation of the Ce(IV)-Co(III) complex and the induced electron transfer to Co(III), being thus consistent with a mechanism in which C-C fragmentation and the two acts of electron transfer to the metal ion centers are synchronous, or very nearly so. This is represented by Scheme I.

Despite evidence that the two oxidizing centers operate in concert, coordinated Co(III) does not facilitate attack by Ce(IV), for the uncomplexed hydroxy acids are found to react 10^2-10^3 times as rapidly as their $(NH_3)_5Co^{III}$ derivatives under comparable conditions. This is, in substantial part, an electrostatic effect, analogous to that described for the Ce(IV) reaction of cobalt(III)-bound oxalate.[3a] When, however, the two reaction centers are separated by a more extended system of bonds, i.e., by an aromatic ring, rates at which the ligand and its Co(III) complex are attacked become similar.[2b,c]

Finally, it is of interest that, although both Cr(V) and Cr(VI) react readily with the mandelato complex, yields of Co^{2+} are only 20-30%. This is in accord with the ability of these oxidants to undergo either one- or two-electron reduction and suggests that the latter mode is predominant with both oxidation states under our conditions. Treatment with thallium(III), which ordinarily functions solely as a two-electron oxidant, yields no detectable Co^{2+}.[15]

Acknowledgment. Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also wish to thank Professors Michael Ardon and Henry Taube for helpful comments.

Registry No. I, 34464-03-4; II, 73543-61-0; III, 47253-58-7; $C_6H_5C(O)COOCo(NH_3)_5^{2+}$, 49861-82-7; Ce^{4+}, 16065-90-0; bis(2-hydroxy-2-ethylbutyrato)oxochromate(V), 75476-70-9; $K_2Cr_2O_7$, 7778-50-9; benzaldehyde, 100-52-7; benzophenone, 119-61-9; Co^{2+}, 22541-53-3; CO_2, 124-38-9; Ce^{3+}, 18923-26-7.

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(15) An analogous instance of induced electron transfer involving the action of Fe(III) on complexes of Cr(III), yielding Fe^{2+} and Cr^{2+}, has been described by J. J. Espenson and A. Bakac, *J. Am. Chem. Soc.*, **102**, 2488 (1980).

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Electron Transfer. 47. Deteriorative Processes in Electron-Transfer Catalysis[1]

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Europium(II) reductions of (pyridine)pentaamminecobalt(III), $py(NH_3)_5Co^{III}$, in the presence of the very powerful catalysts derived from 2,4-pyridinedicarboxylic acid yield kinetic plots showing marked departures from those exponential curves expected if the concentration of catalyst were to remain constant throughout a run. The observed behavior has been shown to correspond to a superposition, onto the primary catalyzed reaction, of two deteriorative processes, both involving the radical intermediate cat·, which results from one-electron reduction of the catalyst. The first of these is a bimolecular disproportionation of the radical; the second is a reaction with an additional Eu^{2+} ion, yielding an unreactive dihydro derivative, $catH_2$. Consideration of the kinetic data, in conjunction with estimated formal potentials of the catalysts, allows calculation of specific rates for the attrition reactions for the several catalysts. Rate constants for disproportionation of the radicals derived from the 2,4 diacid and its methyl ester exceed 10^8 M^{-1} s^{-1}; i.e., the values are slightly below the diffusion-controlled limit for bimolecular reactions. Specific rates for "overreduction" of the radicals by reaction with Eu^{2+} fall in the range 70-400 M^{-1} s^{-1}, about one-tenth the rates for one-electron reductions of the parent aromatics. N-Methylation of the 2,4 diacid greatly improves its catalytic recycling properties without affecting its activity in the medium employed, for this alteration retards attrition by overreduction sixfold and reduces disproportionation to an undetectable level. N-Methylation of the dimethyl ester of this acid yields compound V, which is found to be the most active electron-transfer catalyst of this type thus far prepared. Under conditions of use, however, it suffers deterioration unusually rapidly.

Catalysis of electron-transfer reactions by unbound aromatics has been shown to proceed by preliminary reduction of the catalyst to a radical intermediate, cat·, which then reacts with the oxidant.[2] Earlier reports dealing with this type of catalysis pointed out that such catalysts may deteriorate with use.[2,3] It was further found that degrees of deterioration among different catalysts may vary widely, and evidence was presented[4] that catalytic attrition occurs when the radical

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(1) Sponsorship of this work by the National Science Foundation is gratefully acknowledged.

(2) See, for example: (a) C. Norris and F. Nordmeyer, *J. Am. Chem. Soc.*, **93**, 4044 (1971); (b) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *ibid.*, **99**, 1073 (1977).

(3) (a) J. R. Barber, Jr., and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 4045 (1971); (b) M. R. Loar, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, **17**, 3689 (1978).

(4) C. A. Radlowski, P.-W. Chum, L. Hua, J. Heh, and E. S. Gould, *Inorg. Chem.*, **19**, 401 (1980).

0020-1669/81/1320-0211$01.00/0

intermediate undergoes disproportionation (eq 1) or "overreduction" (eq 2) to an inactive two-electron product, rather than direct reaction with the primary oxidant.

$$2\mathrm{cat}\cdot \xrightarrow{2\mathrm{H}^+} \mathrm{cat} + \mathrm{catH}_2 \qquad (1)$$

$$\mathrm{cat}\cdot + \mathrm{M}^{2+} \xrightarrow{2\mathrm{H}^+} \mathrm{catH}_2 + \mathrm{M}^{3+} \qquad \mathrm{M} = \mathrm{Eu, V} \qquad (2)$$

In the present study a number of reactions in which catalytic deterioration is particularly marked are examined in greater detail. We have used a single reductant, Eu^{2+}, and a single oxidant, $Co(NH_3)_5py^{3+}$, throughout, but have selected several of the most effective catalysts thus far reported. Although our results, in general, confirm the notion that the most powerful electron-transfer catalysts are also the most fragile, we find that, with suitable substitution, very active catalysts may be stabilized toward deteriortion without proportionate loss in effectiveness.

Experimental Section

Materials. (Pyridine)pentaamminecobalt(III) perchlorate, $Co(NH_3)_5py(ClO_4)_3$, the primary oxidant,[5] and solutions of europium(II)[6] were prepared as described. Of the catalysts used, 2,4-pyridinedicarboxylic acid (a K & K product) was recrystallized from hot water three times before use, the dimethyl ester of this acid was prepared by the method of Meyer,[7] and 4-carbamoyl-1-(carboxymethyl)pyridinium perchlorate ($Inic^+–CH_2COOH)(ClO_4^-)$ was prepared by the method of Craig and co-workers.[8]

N-Methylation of dimethyl 2,4-pyridinedicarboxylate was carried out by treatment of the ester with a threefold excess of methylfluorosulfonate (Aldrich "Magic Methyl") (hood!) at room temperature,[9] allowing the mixture to stand 3 h and destroying the unreacted fluorosulfonate by addition of methanol or water, which, after 2 h, was removed in vacuo. ^{13}C NMR (H_2O):[10] δ 163.85 (C═O); 160.86, 151.29, 146.42, 130.54 (ring carbons); 55.87, 55.25 (OCH_3's); 50.21 ($^+NCH_3$).

The N-methylated diester, V, was converted to the corresponding diacid, IV, by refluxing 10 h with 0.5 M $HClO_4$ and then removing the water by rotary evaporation. ^{13}C NMR (H_2O): δ 164.82, 164.75 (C═O's); 161.84, 150.98, 147.20, 147.14, 130.60 (ring carbons); 50.14 ($^+NCH_3$). Despite several attempts, neither the diacid nor its methyl ester was obtained as a crystalline perchlorate. Concentrations of these catalysts were regulated by taking known weights of the nonmethylated diester, assuming the N-methylation[9] and ester hydrolysis (where carried out) to be quantitative, and diluting to appropriate volumes. Master solutions of the ester catalysts were prepared in anhydrous methanol.

Rate Measurements. Progress of the reactions was monitored by measuring decreases in the absorbance at the low-energy Co(III) maximum, 475 nm, by using a Cary 14 recording spectrophotometer.[2b,6b] Reactions were carried out in 1.2 M $HClO_4$ at 25.0 ● 0.2 °C. Measurements were made with $[Eu^{2+}]/[Co^{III}]$ greater than 5.0, with a measured quantity of Eu^{3+} also present to simplify the kinetic treatment (see following section). The resulting kinetic traces were severely distorted from first-order curves but, at the same time, did not resemble second-order plots. Apparent half-life periods steadily increased during the course of each run, and, in most cases, the catalyzed component of the reaction virtually ceased well before all Co(III) was exhausted, leaving only the very slow uncatalyzed reaction ($k = 0.083\ M^{-1}\ s^{-1}$).[6b] These distortions could be shown to reflect loss of catalyst rather than adventitious loss of Eu^{2+}, for when the corresponding reactions were carried out under analogous conditions with ethylene glycol diisonicotinate, a catalyst known to resist deterioration,[4] good exponential decay curves were obtained.

The kinetic traces obtained with the more reactive catalysts could be shown to correspond to a superposition, onto the primary pseudo-first-order reaction, of a uni- or bimolecular decay of the catalyst or a combination of the two modes of decay. Rate constants for the decay processes were estimated by a nonlinear least-squares treatments of the absorbance data, minimizing the function $[(A_0/A_t)_{\mathrm{obsd}} - (A_0/A_t)_{\mathrm{calcd}}]^2$, where the A values refer to absorbances at the beginning of the reaction and at time t, and the calculated ratios were obtained from one of three integrated rate expressions (see below). Initially, individual refinements were carried out for each run, but final refinements utilized data for all runs with a given catalyst.

The *N*-methyl diester, V, was a particularly powerful catalyst, with reactivity at the 10^{-6} M level comparable to that of the 2,4 diacid at the 10^{-5} M level. However, decay of this catalyst, in reactions with Eu^{2+} in excess, was so rapid that only a small portion of the catalytic component could be detected. Experiments carried out with Co(III) in excess yielded pseudo-first-order decay curves, albeit with some distortion. Rate constants, extrapolated to zero time, were proportional to catalyst concentration ($k_{\mathrm{obsd}} = 2 \times 10^4$ (cat) at 25 °C), leading[2b] to the very high, but approximate, k_1 value $2 \times 10^4\ M^{-1}\ s^{-1}$.

Results and Discussion

Earlier studies[2,11] have demonstrated the catalytic mechanism in these systems to be sequence 3. Application of the

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

steady-state approximation to the radical intermediate leads to rate law 4, in which the term containing k_{un} pertains to the

$$\mathrm{rate} = \frac{k_1k_2[\mathrm{Co^{III}}][\mathrm{Eu}^{2+}][\mathrm{cat}]}{k_{-1}[\mathrm{Eu}^{3+}] + k_2[\mathrm{Co^{III}}]} + k_{\mathrm{un}}[\mathrm{Co^{III}}][\mathrm{Eu}^{2+}] \qquad (4)$$

uncatalyzed component. In cases where $[Eu^{2+}] \gg [Co^{III}]$ and excess Eu^{3+} is added, the specific rate for the catalyzed reaction, k_{cat}, may be written as eq 5. For a given run with

$$k_{\mathrm{cat}} = \frac{(\mathrm{rate})_{\mathrm{cat}}}{[\mathrm{Co^{III}}]} = \frac{k_1k_2[\mathrm{Eu}^{2+}][\mathrm{cat}]}{k_{-1}[\mathrm{Eu}^{3+}]} \qquad (5)$$

negligible deterioration of catalyst, this expression is very nearly constant, leading to the exponential kinetic curves observed in the past with the more robust catalysts.[2b] In the present study, however, gradual loss of catalyst must also be taken into account. Representative kinetic data from runs with two different catalysts are given in Table I.

Two deteriorative processes may be considered: the first bimolecular in catalyst (specific rate k_{D2}) (eq 6); the second unimolecular (specific rate k_{D1}) (eq 7). These lead, respectively, to the integrated forms (8) and (9), whereas the rather

$$\frac{-\mathrm{d[cat]}}{\mathrm{d}t} = k_{\mathrm{D2}}[\mathrm{cat}]^2 \qquad (6)$$

$$\frac{-\mathrm{d[cat]}}{\mathrm{d}t} = k_{\mathrm{D1}}[\mathrm{cat}] \qquad (7)$$

$$\ln \frac{[\mathrm{Co^{III}}]_0}{[\mathrm{Co^{III}}]_t} = \frac{k_{\mathrm{cat}}}{k_{\mathrm{D2}}[\mathrm{cat}]_0} \ln\,(1 + k_{\mathrm{D2}}[\mathrm{cat}]_0t) + k_{\mathrm{u}}[\mathrm{Eu}^{2+}]t \qquad (8)$$

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

[6] (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).

[7] H. Meyer and H. Tropsch, *Monatsh. Chem.*, **35**, 189 (1914).

[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] R. W. Alder, *Chem. Ind.* (*London*), 983 (1973). Attempted N-methylation by the procedure of H. Meyer, *Monatsh. Chem.*, **24**, 199 (1903), in which an aqueous solution of the sodium salt is treated with methyl iodide, yielded only minor amounts of methylated products. Treatment of the diester with dimethyl sulfate at 110 °C (T. J. van Bergen and R. M. Kellogg, *J. Am. Chem. Soc.*, **94**, 8451 (1972)) resulted in some N-methylation but produced substantial quantities of tarry materials.

[10] NMR spectra were taken on a Varian FT-80 instrument (20 MHz). Chemical shift data are in ppm in relation to external Me_4Si. Spectra of the N-methylated diester and the corresponding diacid exhibited no resonances attributable to carbon-containing impurities.

[11] Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **16**, 2516 (1977).

$$\ln \frac{[\mathrm{Co^{III}}]_0}{[\mathrm{Co^{III}}]_t} = -\frac{k_{\mathrm{cat}}}{k_{\mathrm{D1}}}(1 - e^{-k_{\mathrm{D1}}t}) + k_{\mathrm{u}}[\mathrm{Eu^{2+}}]t \qquad (9)$$

more elaborate expression (eq 10) results from a combination

$$\ln \frac{[\mathrm{Co^{III}}]_0}{[\mathrm{Co^{III}}]_t} = -\frac{k_{\mathrm{cat}}}{k_{\mathrm{D2}}} \ln \frac{k_{\mathrm{D1}}/[\mathrm{cat}]_0}{\left(\dfrac{k_{\mathrm{D1}}}{[\mathrm{cat}]_0} + k_{\mathrm{D2}}\right)e^{k_{\mathrm{D2}}t} - k_{\mathrm{D2}}} - \frac{k_{\mathrm{cat}k\mathrm{D1}}t}{k_{\mathrm{D2}}} + k_{\mathrm{u}}[\mathrm{Eu^{2+}}]t \qquad (10)$$

of the two processes. In each of these, the uncatalyzed component (the k_u term) is included.

Note that eq 6 reflects the disproportionation reaction (eq 1) with k_{D2}, which remains constant for a given run, linearly related to k_{disp} (eq 11), where k_1 and k_{-1} pertain to steps in

$$k_{\mathrm{D2}} = {}^1\!/_2 k_{\mathrm{disp}}\left(\frac{k_1[\mathrm{Eu^{2+}}]}{k_{-1}[\mathrm{Eu^{3+}}]}\right)^2 \qquad (11)$$

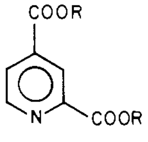
the catalytic mechanism (3).[12] Similarly, eq 7 is related to catalytic deterioration by overreduction, k_{OR} (eq 12).

$$k_{\mathrm{D1}} = k_{\mathrm{OR}}\frac{k_1[\mathrm{Eu^{2+}}]^2}{k_{-1}[\mathrm{Eu^{3+}}]} \qquad (12)$$

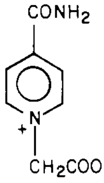
Table I. Representative Kinetic Data for Catalyzed Europium(II) Reductions of py(NH$_3$)$_5$Co^{III} [a,b]

	$[\mathrm{Co^{III}}]_0/[\mathrm{Co^{III}}]_t$	
time, s	obsd	calcd
A. Catalyst: 4-Carbamoyl-1-(carboxymethyl)pyridinium (III) (3.0 × 10^{-5} M)		
0	1.000	1.000
20	1.106	1.176
30	1.157	1.247
40	1.214	1.311
50	1.278	1.370
60	1.330	1.425
70	1.389	1.477
80	1.423	1.527
90	1.506	1.575
100	1.524	1.621
110	1.603	1.666
130	1.712	1.752
150	1.812	1.836
160	1.866	1.878
180	1.984	1.960
200	2.08	2.04
B. Catalyst: *N*-Methyl-2,4-pyridinedicarboxylic acid (IV) (1.00 × 10^{-6} M)		
0	1.000	1.000
20	1.126	1.121
30	1.202	1.185
40	1.263	1.252
50	1.344	1.320
60	1.420	1.393
70	1.488	1.467
80	1.563	1.545
90	1.645	1.625
100	1.736	1.708
120	1.894	1.882
150	2.16	2.17
170	2.36	2.37
200	2.60	2.70
220	2.78	2.94
250	3.05	3.32

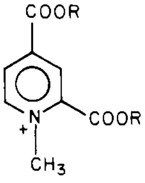
[a] Reactions carried out at 25 °C in 1.2 M HClO$_4$. [b] $[\mathrm{Co^{III}}]_0$ = 2.00 × 10^{-3} M; [Eu^{2+}] = 0.020 M; [Eu^{3+}] = 0.100 M. [c] For part A, ratios were estimated by taking values of k_1k_2/k_{-1}, $k_{\mathrm{disp}}\cdot(k_1/k_{-1})^2$, and $k_{\mathrm{OR}}(k_1/k_{-1})$ from Table II, calculating k_{cat}, $k_{\mathrm{D_2}}$, and $k_{\mathrm{D_1}}$ as indicated in eq 5, 11, and 12, and substituting into eq 10 (see text). For part B, ratios were estimated by taking values of k_1k_2/k_{-1} and $k_{\mathrm{OR}}(k_1/k_{-1})$ from Table II, calculating k_{cat} and $k_{\mathrm{D_1}}$ as indicated in eq 5 and 12, and substituting into eq 9 (see text).



I, R = H
II, R = CH$_3$



III



IV, R = H
V, R = CH$_3$

Reactions in the presence of catalysts I–III, which are devoid of an *N*-methyl group, are found to conform reasonably to eq 8. Moreover, values of k_{cat}, obtained by nonlinear least-squares refinements of absorbance data for individual runs, are very nearly proportional to the quotient [Eu^{2+}][cat]/[Eu^{3+}], thus allowing a preliminary estimate of k_1k_2/k_{-1} in eq 5. However, in each case, plots of k_{D2}, obtained from these individual refinements, vs. [Eu^{2+}]^2/[Eu^{3+}]^2 are significantly curved, with attrition at low catalyst concentrations more severe than can be accounted for by a bimolecular decay process alone, thus indicating an accompanying deterioration process exhibiting a lower order in catalyst, i.e., some unimolecular attrition. The final refinement procedure for each of the three catalysts therefore employed an integrated expression of type 10, but the latter was modified to accommodate a range of concentrations of Eu^{2+}, Eu^{3+}, and catalyst by substituting eq 5, 11, and 12 for k_{cat}, k_{D2}, and k_{D1}. In this refinement, then, known concentrations of reagents and catalyst were entered, and values of k_1k_2/k_{-1}, $k_{disp}(k_1/k_{-1})^2$, and $k_{OR}(k_1/k_{-1})$ were allowed to vary while minimizing the function $[(A_0/A_t)_{\mathrm{obsd}} - (A_0/A_t)_{\mathrm{calcd}}]^2$, where the absorbances (A values) at 475 nm are taken to be proportional to [Co^{III}].[13] Values of these adjustable parameters giving the best agreement between calculated and observed reaction curves for all runs are entered in Table II. Calculated and observed changes for a typical

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(12) The factor $^1/_2$ in eq 11 reflects the inactivation of one of the two radicals participating in an act of disproportionation, the other being returned to the catalyst pool. A more detailed treatment of these interrelationships appears in an earlier work.[4]

(13) More specifically, the equation used in the final refinement was

$$\ln \frac{[\mathrm{Co^{III}}]_0}{[\mathrm{Co^{III}}]_t} = -\frac{AX}{BY} \ln \frac{CZ/[\mathrm{cat}]_0}{\left(\dfrac{CZ}{[\mathrm{cat}]_0} + BY\right)e^{BYt} - BY} - \frac{ACXZt}{BY} + k_{\mathrm{u}}[\mathrm{Eu^{2+}}]t$$

for reactions catalyzed by compounds I, II, and III and

$$\ln \frac{[\mathrm{Co^{III}}]_0}{[\mathrm{Co^{III}}]_t} = -\frac{AX}{CZ}(1 - e^{-AXt}) + k_{\mathrm{u}}[\mathrm{Eu^{2+}}]t$$

for reactions catalyzed by IV. Values of A, B, and C which were entered were derived from the reagent concentrations $A = [\mathrm{Eu^{2+}}][\mathrm{cat}]_0/[\mathrm{Eu^{3+}}]$, $B = ([\mathrm{Eu^{2+}}]/[\mathrm{Eu^{3+}}])^2$, and $C = [\mathrm{Eu^{2+}}]^2/[\mathrm{Eu^{3+}}]$, whereas the parameters X, Y, and Z, which were allowed to vary, corresponded to the composite kinetic parameters indicated by $X = k_1k_2/k_{-1}$, $Y = {}^1/_2k_{\mathrm{disp}}(k_1/k_{-1})^2$, and $Z = k_{\mathrm{OR}}(k_1/k_{-1})$ with k_u the specific rate for the uncatalyzed reduction and t the reaction time. Copies of the nonlinear least-square program used (subtitled GNLLS) may be obtained from J.W.R.

Table II. Catalytic Deterioration in Catalyzed Europium(II) Reductions of (Pyridine)pentaamminecobalt(III), $py(NH_3)_5Co^{III}$: Composite Rates and Kinetic Deterioration Parameters[a]

catalyst	n[b]	$10^4 k_1k_2/k_{-1}$, $M^{-1}\ s^{-1}$	$10^4 k_{disp}(k_1/k_{-1})^2$, $M^{-1}\ s^{-1}$	$k_{OR}(k_1/k_{-1})$, $M^{-1}\ s^{-1}$
2,4-pyridinedicarboxylic acid (I)	77	2.30 ± 0.07	5.2 ± 0.8	3.2 ± 0.1
dimethyl 2,4-pyridinedicarboxylate (II)	70	2.5 ± 0.1	9.8 ± 2.0	2.6 ± 0.1
4-carbamoyl-1-(carboxymethyl)pyridine (III)	84	0.089 ± 0.010	1.58 ± 0.40	0.049 ± 0.004
N-methyl-2,4-pyridinedicarboxylic acid (IV)	110	2.05 ± 0.10	<0.9	0.59 ± 0.06

[a] Reactions were carried out in 1.2 M $HClO_4$ at 25 °C. Rate constants k_1, k_{-1}, and k_2 refer to steps in reaction sequence 3. k_{disp} is the specific rate of disproportionation of the catalyst radical cat· (eq 1), and k_{OR} is the specific rate of overreduction of this radical by Eu^{2+} (eq 2). Values of these parameters were obtained by nonlinear least-squares refinements of kinetic data (see text and ref 13). [b] Number of experimental points included in the refinement.

Table III. Estimated Specific Rates for Catalytic Deterioration Processes[a]

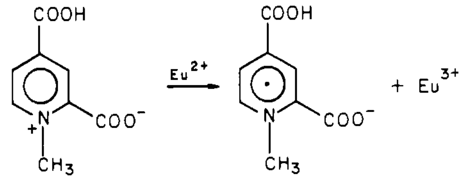
catalyst	$E°$, V[b]	log (k_1/k_{-1})[c]	k_{disp},[d] $M^{-1}\ s^{-1}$	$10^{-2}k_{OR}$,[e] $M^{-1}\ s^{-1}$
2,4-pyridinedicarboxylic acid (I)	−0.500	−2.05	7×10^8	4
dimethyl 2,4-pyridinedicarboxylate (II)	−0.495	−1.96	8×10^8	2
N-methyl-2,4-pyridinedicarboxylic acid (IV)	−0.502	−2.08	$<6 \times 10^7$	0.7

[a] Reactions at 25 °C in 1.2 M $HClO_4$. [b] Potentials estimated from values of k_1k_2/k_{-1} as described by Fanchiang.[14] [c] k values refer to one-electron reduction of catalyst by Eu^{2+} and its reverse. $E°$ for Eu^{2+}/Eu^{3+} is taken as −0.379 V (G. Biedermann and H. R. Silber, *Acta Chem. Scand.*, 27, 3751 (1973)). [d] Specific rate for $2\text{cat}\cdot \xrightarrow{2H^+} \text{cat} + \text{cat}H_2$. [e] Specific rate for the reaction $\text{cat}\cdot + Eu^{2+} \xrightarrow{2H^+} \text{cat}H_2 + Eu^{3+}$.

run (with catalyst III) are compared in Table IA.

In the reactions catalyzed by *N*-methyl-2,4-pyridinedicarboxylic acid (IV), catalytic attrition is less severe and conforms closely to eq 9, which describes deterioration by overreduction alone. Application of eq 10, which accommodates two deteriorative paths, to the data for this catalyst did not improve agreement between calculated and observed curves. Table IB compares calculated and observed changes for a run employing this N-methylated diacid.

Note (Table II) that N-methylation has scarely affected the catalytic activity of the 2,4 diacid, for the k_1k_2/k_{-1} values (which measure catalytic effectiveness under usual conditions) are virtually the same for catalysts I and IV. At the same time, however, this structural alteration has made the molecule much more robust in the reaction medium employed. Overreduction of the ring has been retarded sixfold, whereas disproportionation, which is ordinarily the principal mode of attrition, has become undetectable. Whether this remarkable improvement in recycling characteristics is a thermodynamic effect, linked to a strongly negative two-electron reduction potential for this catalyst, or whether it is kinetic in origin, reflecting an unusually sluggish disproportion of the *N*-methyl 2-carboxylate form of the radical (VI) (see eq 13) (which is the principal form of the intermediate from the methylated diacid, but not from other catalysts in this series) is, at present, an open question.



(13)

IV VI

In contrast, catalytic attrition of the *N*-methyl diester V is found to be extraordinarily severe. In experiments with Eu^{2+} in excess, this catalyst is depleted very early in each run, and observed catalytic curves are found to be unusually shallow with rates rapidly diminishing to the uncatalyzed value. Although this very rapid decay rules out obtaining values of the quotient k_1k_2/k_{-1} (which represents the relative effectiveness of the catalyst as it is usually used[2b]) directly, experiments with Co(III) in excess allow us to estimate[2b] k_1 as 2×10^4 $M^{-1}\ s^{-1}$ (25 °C). If, in common with other catalysts of this type,[4] k_2/k_{-1} is taken to be about 8, we obtain a value of 1.6×10^5 for k_1k_2/k_{-1}. The latter is the highest value reported for this composite parameter. The N-methylated diester then is the most powerful electron-transfer catalyst of this type thus far prepared, but, at the same time, it is among the most fragile.

Conversion of the deterioration parameters in Table II to the specific rates at which the radical intermediate undergoes dipproportionation (k_{disp}) or overreduction (k_{OR}) requires knowing the ratio k_1/k_{-1}, which, in turn, reflects the standard potentials for one-electron reductions of the catalysts. Although cyclic voltammograms of a number of catalysts of this type in 1 M $HClO_4$ have been measured,[14] the plurality of reaction paths open to the radicals complicates a quantitative interpretation. However, values of k_1k_2/k_{-1}, in conjunction with an extrathermodynamic relationship which has been found[15] to link the effectiveness of pyridine-derived catalysts with their standard potentials, allow us to estimate the potentials for catalysts I, II, and IV listed in Table III, as well as the values of k_{disp} and k_{OR}. This treatment is not applied to catalyst III, the behavior of which has been shown to be complicated by "homoallylic" type interactions.[4,8b]

The estimated rate constants for disproportionation (k_{disp}) are slightly below the diffusion-controlled limit in water at 25 °C and fall into the range of decay constants reported for 4-substituted pyridinyl radicals in aqueous systems.[16] More noteworthy, however, are the specific rates for overreduction (k_{OR}), which refer to the reaction of Eu^{2+} with the radical cat·. It has been shown earlier[4] that substituted pyridinyl radicals of the type here considered are significantly stronger oxidants than the aromatics from which they are derived. Nevertheless, they are found to react with Eu^{2+} only about one-tenth as rapidly as the parent aromatics (which exhibit k_1 values near 2×10^3 $M^{-1}\ s^{-1}$).[14] This difference suggests the imposition of a greater reorganizational barrier in accepting the second

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

(15) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978). The relationship derived by these authors, applicable to catalyzed reductions of $py(NH_3)_5Co^{III}$, is $\log (k_1k_2/k_{-1}) = (E°_{Cat} - E°_M)F/2.3RT + 3.81 - 5.17E°_{Cat}$, where the $E°$ values refer to the catalyst and the metal-center reductant and F is the value of the Faraday.

(16) (a) E. M. Kosower, A. Teuerstein, H. D. Burrows, and A. J. Swallow, *J. Am. Chem. Soc.*, **100**, 5185 (1978). (b) See, also, E. Hayon and M. Simic, *ibid.*, **95**, 1029 (1973).

electron than acquiring the first. More specifically, we suspect that the radical, like the parent pyridine, is essentially aromatic in character, with all bonds within the ring nearly the same length, whereas in the transition state leading to the two-electron product, the distinction between single and double bonds ultimately appearing in the dihydro ring has begun to develop.

In summary, by considering the distortions in the kinetic curves obtained from catalyzed electron-transfer reactions, we have estimated specific rates for the individual processes resulting in deterioration of the catalysts. We have further found that N-methylation of dimethyl 2,4-pyridinedicarboxylate yields an extraordinarily active, although fragile, catalyst, whereas methylation of the parent dicarboxylic acid results in a catalyst unusually resistant to attrition without sacrifice of its reactivity. For a more detailed picture of the differences between the individual catalysts under reducing conditions, it is likely that electrochemical studies in cobalt-free systems will be informative. Continuing work is in this direction.[17,18]

Acknowledgment. We are indebted to Professors John Gordon and Milton Manes for valuable discussions.

Registry No. I, 499-80-9; II, 25658-36-0; III, 72121-35-8; IV, 75475-96-6; V, 65878-79-7; py$(NH_3)_5Co^{III}$, 31011-67-3; Eu^{II}, 16910-54-6.

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(17) A referee asks whether processes analogous to those described are present in biological electron-transport chains. Fanchiang[2b] has noted points of similarity and also has indicated[18] briefly where substantial areas of difference lie.

(18) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1138 (1978).

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Coordination Rearrangement Controlled Electron Transfer. 5. Formation of V(III)-Ti(IV) and Ti(III)-Ti(IV) Binuclear Complexes in the Cross Reaction of Ti(hedta) and VO(hedta)$^-$ [1]

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A twist mechanism or dissociative process involving rupture of a carboxylato–Ti^{III} bond in Ti(hedta)(H_2O) limits the rate of oxidation of Ti(hedta)(H_2O) by VO(hedta)$^-$ (hedta^{3-} is the ligand *N*-(hydroxyethyl)ethylenediaminetriacetate). The electron-transfer step is outer sphere; a binuclear species containing Ti(IV) and V(III) appears by a substitution reaction after the electron-transfer step. The limiting redox process is first order in [Ti(hedta)(H_2O)] alone with $k_{obsd} = 73.6 \pm 5.0\ s^{-1}$ (μ = 0.50 (NaCl), pH 5.0, acetate buffer, T = 25.2 °C). Relaxation studies reveal a ring opening of a glycinato fragment of the hedta^{3-} ligand for Ti(hedta)(H_2O)(OH)$^-$ which proceeds by an inverse hydrogen ion pathway ($k_1 = 1.92 \times 10^{-4}\ M\ s^{-1}$) and reverse ring closure ($k_0 = 6.2\ s^{-1}$). A slower monomerization reaction involving a binuclear $Ti^{III}{}_2$(hedta)$_2$ complex is detectable. The monomerization of the binuclear complex saturates in [H_3O^+]. The magnitudes of the kinetic constants support a proton-scavenging mechanism involving a monohydroxy-bridged, strained intermediate with a rate-limiting bond-rupturing process of 0.33 s^{-1}. The formation of a new $Ti^{III}Ti^{IV}$ binuclear complex occurs with a second-order constant of $(3.12 \pm 0.42) \times 10^2\ M^{-1}\ s^{-1}$ in competition with the dominant outer-sphere cross reaction involving Ti(hedta)(H_2O) and VO(hedta)$^-$. The species appears blue to the eye ($\lambda_{max} \simeq 800$ nm, $\epsilon = 47\ M^{-1}\ cm^{-1}$); the identical $Ti^{III}Ti^{IV}$(hedta)$_2$ complex may be prepared by autoxidation of Ti(hedta)(H_2O). The $Ti^{III}Ti^{IV}$ ion is thermodynamically unstable at pH 4.0. Above pH 4.0 the dissociation of $Ti^{III}Ti^{IV}$ occurs by a first-order process ($k \simeq 0.14\ s^{-1}$) producing the redox-active isomer of Ti(hedta)(H_2O). $Ti^{III}Ti^{IV}$, prepared by combination of thermally equilibrated samples of Ti(hedta)(H_2O) and TiO(hedta)$^-$, forms by a different path dependent only on [Ti(IV)] ($k = 3.4 \pm 0.1\ s^{-1}$). The initial products of the Ti(hedta)(H_2O)/VO(hedta)$^-$ cross reaction are TiO(hedta)$^-$ and V(hedta)(H_2O). These products combine at a rate of 23 $M^{-1}\ s^{-1}$ to form a third binuclear species $Ti^{IV}V^{III}$(hedta)$_2$ having a charge-transfer maximum at 453 nm ($\epsilon = (3.8 \pm 0.1) \times 10^2\ M^{-1}\ cm^{-1}$). The formation constant for this orange Ti(IV)–V(III) complex is $5.0 \times 10^2\ M^{-1}$ (μ = 0.50 (NaCl), T = 25.0 °C). A binuclear species which contains the reverse oxidation state assignment Ti^{III}–V^{IV} is detected competitively early in the cross reaction with a rate of formation of $(1.23 \pm 0.14) \times 10^4\ M^{-1}\ s^{-1}$. However this species is not the precursor complex of the orange $Ti^{IV}V^{III}$(hedta)$_2$ complex; the Ti^{III}–V^{IV} species is nonproductive for inner-sphere electron transfer.

Introduction

Recent reports have shown a chemistry for Ti(edta)(H_2O)$^-$ as a reducing agent parallel to the features of $Ti(H_2O)_6{}^{3+}$.[2] $Ti(H_2O)_6{}^{3+}$ is the most strongly reducing d^1 aquo ion; the edta^{4-} complex of Ti(III) is even more powerful.[3] A diverse group of inorganic oxidants have been used to determine the mechanistic aspects of reductions with $Ti(H_2O)_6{}^{3+}$. These have included nonmetal acceptors (I_2, $ClO_4{}^-$),[4] simple aquo and oxo cationic oxidants (Hg^{2+}, Fe^{3+}, VO^{2+}, $VO_2{}^+$, $UO_2{}^{2+}$),[5,6] outer-sphere oxidants ($Co(NH_3)_6{}^{3+}$, $Co(bpy)_3{}^{3+}$, $Co(terpy)_2{}^{3+}$, $Ru(NH_3)_6{}^{3+}$, $Ru(NH_3)_5Cl^{2+}$),[7,8] and Co(III) oxidants which have a potential bridging ligand in $(NH_3)_5CoX^{3-n}$ (X^{n-} = F^-,

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(1) Parts of this paper were presented previously at the National Meeting of the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979.

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