PDTA > CyDTA. This order is not unexpected since $CoCyDTA^-$ is known[12] to be a weaker oxidizing agent than $CoEDTA^-$. The equilibrium constants for these reactions are in agreement with the rate data. The decrease in k_{-3} values can be attributed partly to the greater size of the CyDTA chelate, resulting in a greater tunneling distance and thus a lower probability for barrier penetration.[26] The rate constant for the reduction of $CoEDTA^-$ by $Fe(CN)_5PPh_3{}^{3-}$ is explained by a decrease in electrostatic interaction and a weaker driving force (lower $\Delta E°$) for the reaction.

Registry No. $Co^{II}CyDTA$, 65802-32-6; $Co^{II}PDTA$, 52021-76-8; $Co^{II}EDTA$, 11063-56-2; $Fe(CN)_6{}^{3-}$, 13408-62-3; $Fe(CN)_5(Ph_3P)^{2-}$, 22548-72-7.

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Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer. 32. Synergism in Redox Catalysis, Leading to Four-Membered in Vitro Electron-Transport Chains[1]

Y.-T. FANCHIANG and EDWIN S. GOULD*

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Several pairs of redox catalysis have been found to exhibit catalytic effectiveness, for the Eu^{2+} reduction of $Co(en)_3{}^{3+}$, considerably more marked than the sum of the individual catalyses. One catalyst in each pair has a donor site which may function as a lead-in group and appears to react with Eu^{2+} via an inner-sphere process; the other member may participate only in outer-sphere electron transfer. The proposed catalytic sequence, illustrated for the combination of isonicotinamide (I) and methylviologen (V), leads to a rate law (eq 4 in the text) corresponding to that observed. Specific rates for some

$$Eu^{2+} + I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Eu^{3+} + I\cdot$$

$$I\cdot + V \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I + V\cdot$$

$$V\cdot + Co(III) \xrightarrow{k_3} V + Co^{2+}$$

of the steps comprising each of the catalytic sequences have been obtained from studies on single-catalyst systems, whereas the ratio k_2/k_{-2} is determined by the standard potentials of the catalysts. For most sets of conditions here examined, the specific rate of the overall reaction approaches $k_1k_2k_3/k_{-1}k_{-2}$. The observed specific rate for the reaction, as catalyzed by the isonicotinamide–methylviologen couple, is found to be in reasonable agreement with that obtained by combination of the known specific rates for the individual steps, both in 1 M $HClO_4$ and in acetate buffer. Ratios of reactant to catalyst in the latter medium can be adjusted to estimate a value of k_2 which, in conjunction with the E_0 values for the catalysts in this medium, allows assignment of a specific rate to each step in the sequence. Radicals derived from both catalysts react rapidly and completely with $Co(en)_3{}^{3+}$. The enhanced effectiveness of the two catalysts in tandem arises because the radical from the outer-sphere member (e.g., V·) which attains the greater steady-state concentration, is generated by the action of Eu^{2+} at a lower specific rate than the radical from the inner-sphere member (e.g., I·).

In an earlier report[2] we pointed out the formal analogy between in vivo electron-transport chains and electron-transfer reactions catalyzed by external organic species in solution. The latter processes, however, may at best be considered highly abbreviated models of the bio systems, for they feature, aside from the metal ion centers which furnish the driving force for the net reaction, only a single catalytic intermediary.

The present communication deals with several systems in which the in vitro electron-transfer chain has been expanded to four members by inclusion of two catalysts exhibiting a combined action greatly exceeding the sum of their individual effects. The "outer-members" of the chains, $Co(en)_3{}^{3+}$ and

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Table I. Catalyzed Reductions of $Co(en)_3^{3+}$ by Eu^{2+} (25 °C)

Bridging catalyst (concn, M)	Outer-sphere catalyst (concn, M)	$[H^+]$, M	Rate, $M\ s^{-1} \times 10^{6}$ [a]
None	None	1.0	0.02
		2×10^{-5} [d]	0.02
Isonicotinamide (I)			
(0.0127)	None	1.0	2.3[b]
(0.0186)		2×10^{-5} [d]	4.7[b]
Isonicotinic acid (II) (0.032)	None	1.0	18
N-Methylisonicotinic acid (III) (0.026)	None	1.0	23
4-Pyridineacrylic acid (IV) (0.001 72)	None	1.0	5.4
None	Methylviologen (V) (5.1×10^{-4})	1.0	7.8
None	4,4′-Bipyridyl (VI) (5.6×10^{-4})	1.0	5.0
None	1,2-Bis(4-pyridyl)ethylene (VII)[c] (1.12×10^{-3})	1.0	4.9
Isonicotinamide (0.0127)	Methylviologen (5.1×10^{-4})	1.0	84[b]
(0.0186)	(4.1×10^{-4})	2×10^{-5} [d]	77[b]
Isonicotinic acid (0.032)	Methylviologen (5.1×10^{-4})	1.0	122
N-Methylisonicotinic acid (0.026)	Methylviologen (1.71×10^{-4})	1.0	4×10^{2}
4-Pyridineacrylic acid (0.001 72)	Methylviologen (1.71×10^{-4})	1.0	34
Isonicotinamide (0.0053)	4,4′-Bipyridyl (5.6×10^{-4})	1.0	35
Isonicotinamide (0.0053)	1,2-Bis(4-pyridyl)ethylene (0.001 12)	1.0	131

[a] Reaction progress monitored spectrophotometrically at 465 nm (see ref 2). $[Eu^{2+}] = 0.020$ M. $[Co^{III}] = 0.00167$ M, $[Eu^{3+}] = 0.04$ M unless otherwise indicated. [b] $[Eu^{3+}] = 0.03$ M. [c] For evidence that this catalyst is a trans olefin, see T. Katsumoto, *Bull. Chem. Soc. Jpn.*, **33**, 1376 (1960). [d] $HOAc–OAc^-$ buffer.

Eu^{2+}, are kept the same throughout. The tris chelate, despite its very strong oxidizing potential, is, in the absence of catalysis, one of the most sluggish Co(III) oxidants known. Use of Eu^{2+} as a reductant avoids possible difficulties resulting from metal–catalyst coordination which often arise in d-electron redox systems. The catalysts, which function as inner members of the chains, are chosen from two groups. Those in the first group have donor atoms which may function as lead-in sites; evidence has been presented[3] that these react with reducing metal centers via inner-sphere processes. Catalysts in the second group are devoid of such sites and thus may participate only in outer-sphere electron transfers.[4]

Under favorable conditions it is possible to estimate specific rates, forward as well as reverse, for each step in the chain. A portion of these results have already been presented in preliminary form.[5]

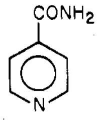
Experimental Section

Materials. Lithium perchlorate[6a] and solutions of europium(II) perchlorate[6bc] were prepared by published procedures. 4-Pyridineacrylic acid and $Co(en)_3(ClO_4)_3$ were available from a previous study.[2] Other catalysts (Aldrich or Alfred Bader products) were used as received.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[2,4,6] All reactions were carried out under nitrogen. Measurements were made both in 1.0 M $HClO_4$ and near pH 5 ($HOAc–OAc^-$ buffer). For the buffered reactions, buffer components were kept relatively dilute (0.05 M) in order to minimize kinetic complications arising from extraneous anion involvement.[7] In most cases $(Eu^{2+})/(Co^{III})$ at the beginning of the reaction exceeded 5, resulting in pseudo-first-order kinetics for the reactions at high acidity and either pseudo-zero- or pseudo-first-order kinetics, depending (vide infra) on the concentration of catalyst, at pH 4.6. All reactions were run at μ near 1.0 ($HClO_4–LiClO_4$ mixtures). Pseudo-first-order reactions were followed to at least 4 half-lives and rate constants were obtained from logarithmic plots of absorbance differences against reaction time; rate constants derived from replicate runs checked to within 7%. Pseudo-zero-order rate constants were obtained from slopes during the first 70% reaction before deviations from zero-order behavior became troublesome; pseudo-zero-order constants from replicate runs checked to within 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Results and Discussion

Table I lists the rates at which $Co(en)_3^{3+}$ is reduced by Eu^{2+} in representative solutions containing (a) no catalyst, (b) several of the bridging catalysts alone, (c) outer-sphere catalysts alone, and (d) catalysts of both types. Although no effort has been made to maximize the effect, the synergistic action of combinations of inner- and outer-sphere catalysts is quite marked.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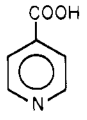
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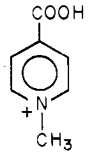
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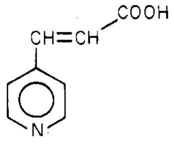
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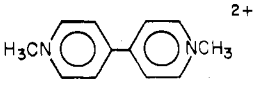
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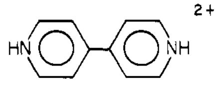
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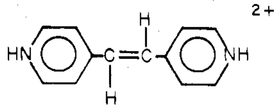

VII

It has been shown[2-4] that although both types of catalyst are reduced to radical species by Eu^{2+}, reductions of the bridging catalysts are 3–100 times as rapid as those of the outer-sphere catalysts. Moreover, in the present study, the bridging catalysts are used at concentrations 5–20 times as great as those for the outer sphere. At the same time, scattered data relating to the potentials for the two types of catalyst indicate that the outer-sphere catalysts used here are stronger oxidizers than the inner by about 150 mV.[8-11] If it is further assumed that thermodynamically favored electron-transfer

Table II. Catalyzed Europium(II) Reductions of $Co(en)_3{}^{3+}$: Kinetic Parameters[a]

Catalyst combination	k_1[b]	k_{-1}[b]	k_3[c]	$k_1k_2k_3/k_{-1}k_{-2}$[d]
Isonicotinamide + methylviologen				
(1 M $HClO_4$)	2.0	5×10^5	5×10^4	1.5×10^2
(pH 4.6)[f]	2.8[d]	4.9×10^6	(5×10^4)[e]	3.5×10^2
Isonicotinamide + 4,4′-bipyridyl	2.0	5×10^5		8.4×10
Isonicotinamide + 1,2-bis(4-pyridyl)-ethylene	2.0	5×10^5		1.8×10^2
Isonicotinic acid + methylviologen	15		5×10^4	3.3×10^2
N-Methylisonicotinic acid + methylviologen	16		5×10^4	3.5×10^2
4-Pyridylacrylic acid + methylviologen	27		5×10^4	3.0×10^2

[a] *k* values (see sequence 1–3) and the ratio $k_1k_2k_3/k_{-1}k_{-2}$ are in $M^{-1}\ s^{-1}$. Reaction temperatures were 25 °C. Reactions were carried out in 1.0 M $HClO_4$ unless otherwise indicated. [b] See ref 2. [c] See ref 4. [d] This work. [e] Reaction of radical of methylviologen with $Co(en)_3{}^{3+}$ assumed to be independent of pH. [f] [HOAc] = [OAc^-] = 0.05 M.

Table III. Kinetic Data for the Europium Reduction of $Co(en)_3{}^{3+}$, as Catalyzed by Combinations of Isonicotinamide (I) and Methylviologen (V) (25 °C)

	$10^2[Eu^{2+}]$, M	$10^2[I]$, M	$10^4[V]$, M	$10^2[Eu^{3+}]$, M	k_{obsd}[c]	k_{calcd}[d]
Pseudo-first-order reductions in 1 M $HClO_4$[a]	2.00	0	0	0	0.002	
	2.00	1.27	0	3.00	0.14	
	2.00	1.20	5.13	3.00	5.0	5.0
	1.00	1.20	5.13	3.00	2.7	2.6
	3.00	1.20	5.13	3.00	6.9	7.7
	2.00	6.00	5.13	3.00	5.0	5.0
	2.00	1.71	5.13	3.00	5.0	5.0
	2.00	1.20	7.70	3.00	6.9	7.7
	2.00	1.20	5.13	2.00	6.9	7.7
	2.00	1.20	5.13	3.00	5.0	5.0
	2.00	1.20	5.13	4.00	4.0	3.8
	1.33	1.20	2.57	3.00	1.9	1.7
Pseudo-first-order reductions at pH 4.6[b]	2.00	0	0	0	0.002	
	2.00	1.86	0	3.00	0.36	
	1.00	1.86	1.66	6.00	1.7	1.7
	2.00	1.86	1.66	6.00	3.2	3.3
	3.00	1.86	1.66	6.00	5.5	5.0
	2.00	0.93	1.66	6.00	2.9	3.3
	2.00	2.78	1.66	6.00	3.6	3.3
	2.00	1.86	3.31	6.00	6.9	6.6
	2.00	1.86	0.83	6.00	1.5	1.7
	2.00	1.86	1.66	3.00	7.7	6.7
	2.00	1.86	1.66	9.00	1.8	2.2
Pseudo-zero-order reductions at pH 4.6[b]	2.00	0.37	2.49	3.00	2.8	2.8
	1.00	0.37	2.49	3.00	1.2	1.4
	2.00	0.25	2.49	3.00	1.9	1.9
	2.00	0.123	2.49	3.00	1.2	0.93
	2.00	0.37	1.66	3.00	1.7	1.9
	2.00	0.37	0.83	3.00	1.1	0.93
	2.00	0.37	2.49	6.00	1.4	1.4
	2.00	0.37	2.49	4.00	2.0	2.1
	2.00	0.37	2.49	2.00	3.5	4.2

[a] $[Co(en)_3{}^{3+}]_0 = 1.67 \times 10^{-3}$ M. [b] $[Co(en)_3{}^{3+}]_0 = 9.85 \times 10^{-4}$ M. $\mu = 1.0$. [c] Pseudo-first-order rate constants ($s^{-1} \times 10^2$) = $(-d[Co^{III}]/dt)[Co^{III}]^{-1}$; pseudo-zero-order rate constants ($M\ s^{-1} \times 10^5$) = $-d[Co^{III}]/dt$. [d] For reactions in 1 M $HClO_4$, k_{calcd} (in $s^{-1} \times 10^2$) = $150 \cdot [Eu^{2+}][V][Eu^{3+}]^{-1}$. For pseudo-first-order reactions at pH 4.6, $k_{calcd} = 6 \times 10^2[Eu^{2+}][V][Eu^{3+}]^{-1}$. For pseudo-zero-order reactions, $k_{calcd} = 45[I][V][Eu^{2+}][Eu^{3+}]^{-1}$ (see text).

reactions between two conjugated organic species are very rapid ($k \sim 10^8\ M^{-1}\ s^{-1}$),[12] the steady-state concentration of the radical derived from the outer-sphere catalyst will be considerably greater than that from the inner sphere. We therefore favor, as the principal catalytic route, a sequence in which the initial act of electron transfer from Eu^{2+} is to the bridging catalyst, but the electron transfer to Co(III) involves the radical from the outer-sphere catalyst.

The proposed mechanism, illustrated for the catalytic combination isonicotinamide (I) and methylviologen (V), is

$$Eu^{2+} + I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Eu^{3+} + I\cdot \tag{1}$$

$$I\cdot + V \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I + V\cdot \tag{2}$$

$$V\cdot + Co(III) \xrightarrow{k_3} Co^{2+} + V \tag{3}$$

Application of the steady-state approximation to radicals I· and V· leads to the rate expression

$$\frac{-d[Co^{III}]}{dt} = \frac{k_1k_2k_3[I][V][Eu^{2+}][Co^{III}]}{k_{-1}k_{-2}[Eu^{3+}][I] + k_2k_3[V][Co^{III}] + k_{-1}k_3[Eu^{3+}][Co^{III}]} \tag{4}$$

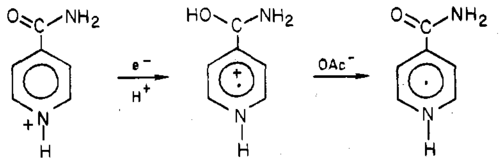
Specific rates for certain of these steps, obtained from earlier studies on single-catalyst systems,[2,4] are listed in Table II.[13,14] From the reduction potentials of isonicotinamide and methylviologen in 1.0 M $HClO_4$,[8] k_2/k_{-2} for the I + V system may be calculated to be 330. Assuming, as above, a very large value for k_2, the first term in the denominator of eq 4 may be shown to predominate in 1 M $HClO_4$ if Eu^{2+} is held in excess, leading to the simplified expression (eq 5) which

$$\frac{-\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \frac{k_1k_2k_3[\mathrm{V}][\mathrm{Eu^{2+}}][\mathrm{Co^{III}}]}{k_{-1}k_{-2}[\mathrm{Eu^{3+}}]} \tag{5}$$

corresponds algebraically (note the zero-order dependence on isonicotinamide) to the observed rate law under these conditions. Representative kinetic data, pertaining to this catalyst pair, both in 1 M $HClO_4$ and in acetate buffer, appear in Table III.

The ratio $k_1k_2k_3/k_{-1}k_{-2}$ for this combination of catalysts in 1 M $HClO_4$ is calculated to be 0.7×10^2 M^{-1} s^{-1}, which may be taken to be in reasonable agreement with our observed rate constant, 1.5×10^2 M^{-1} s^{-1}, when the large uncertainty in k_2/k_{-2} (reflecting the uncertainty in the reduction potential for isonicotinamide[9]) is considered. The other catalyst pairs also follow rate law 5, indicating that for these systems too the first term in the denominator of eq 4 outweighs the others. Values of $k_1k_2k_3/k_{-1}k_{-2}$ for the various combinations, which may be regarded as a measure of catalytic effectiveness under our conditions, are compared in Table II. With $Co(en)_3^{3+}$ in large excess, the second term in the denominator of eq 4 predominates, and the kinetic behavior of the reaction approaches that with the inner-sphere catalyst alone.

When the isonicotinamide–methylviologen couple is used in acetate buffer rather than in 1 M $HClO_4$, its effectiveness is seen to increase, and values of the kinetic parameters (Table II) change appreciably, reflecting principally the conversion of radical VIII to its more powerfully reducing[9,12] conjugate base IX at the higher pH. Associated with this change in medium is a modest increase in k_1, a tenfold increase in k_{-1}, and, of particular interest, a substantial drop in k_{-2}. The latter allows adjustment of reactant concentrations so that the third term in the denominator of eq 4 predominates, whereupon the rate law assumes the form



VIII IX

$pK_A = 1.9$[12]

$$\frac{-\mathrm{d}[\mathrm{Co^{III}}]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{I}][\mathrm{V}][\mathrm{Eu^{2+}}]}{k_{-1}[\mathrm{Eu^{3+}}]} \tag{6}$$

Thus, at low concentrations of isonicotinamide, the catalyzed reaction becomes first order in amide but zero order in Co(III) (Table III). Measurements under such conditions yield the ratio $k_1k_2/k_{-1} = 45$ M^{-1} s^{-1}, whence $k_2 = 8 \times 10^7$ M^{-1} s^{-1}, a value about an order of magnitude less than those pertaining to reactions of pyridine-derived radicals with uncharged acceptors.[12] By using the E_0 value −0.75 V for isonicotinamide in this medium,[13] it is then possible to assign a specific rate to each step in the catalytic sequence:

$$\mathrm{Eu^{2+}} \xrightleftharpoons[\mathrm{Eu^{3+}},\ k_{-1} = 5 \times 10^6]{\mathrm{I},\ k_1 = 2.8} \mathrm{I}\cdot \xrightleftharpoons[\mathrm{I},\ k_{-2} = 7 \times 10^3]{\mathrm{V},\ k_2 = 8 \times 10^7} \mathrm{V}\cdot \xrightarrow[k_3 = 5 \times 10^4]{\mathrm{Co(en)_3}^{3+}} \mathrm{Co^{2+}}$$

I = isonicotinamide; V = methylviologen; k values in M^{-1} s^{-1}

Our measurements on this system under pseudo-first-order conditions (Table III) lead to the empirical rate constant ($=k_1k_2k_3/k_{-1}k_{-2}$) 6×10^2 M^{-1} s^{-1}. Discrepancy between this and the calculated quotient, 4×10^2, probably reflects, in large part, the different medium (1 M *t*-BuOH, no supporting electrolyte) used in the pulse radiolytic experiments on which the value of k_{-1} is based.[9]

In sum, it should be noted that radicals, both of type I· and type V·, react rapidly and completely (necessarily by an outer-sphere path) with $Co(en)_3^{3+}$. The enhanced effectiveness of the two catalysts in tandem arises because V·, the radical with the greater steady-state concentration, is generated by Eu^{2+} (also by an outer-sphere process) at somewhat the lower specific rate. In effect, isonicotinamide, for which an inner-sphere path is preferred,[3] catalyzes the formation of V·, the predominant species reacting with Co(III).

The search for an analogous three-catalyst system is expected to be less straightforward, for the combined effectiveness of the three must exceed not only the sum of the individual catalyses but also the action of any member in conjunction with the combination of the remaining two.

Registry No. I, 1453-82-3; II, 55-22-1; III, 36455-39-7; IV, 5337-79-1; V, 4685-14-7; VI, 46040-54-4; VII, 55326-18-6; Eu^{2+}, 16910-54-6; $Co(en)_3^{3+}$, 14878-41-2.

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(13) Values of k_1 and k_{-1} for isonicotinamide in $HOAc–OAc^-$ buffer are obtained by combination, in a manner analogous to that described,[2] of kinetic data for the $Co(NH_3)_5py^{3+}–Eu^{2+}$ reaction, as catalyzed in this medium by isonicotinamide alone, with pulse radiolytic data pertaining to solutions at pH 6.4–6.7.[9] Bruhlmann and Hayon[12] have shown that neither isonicotinamide nor the radical derived from it undergoes significant shift in protonation equilibrium within the pH range 6.7–4.6.[14] From this treatment, the reduction potential for isonicotinamide in this medium is estimated as −0.748 V, a value which may be regarded as more reliable than the corresponding potential in 1 M $HClO_4$ in view of the more precise radiolytic data obtained at the higher pH.
(14) The reported pK_A of HOAc in 1 M perchlorate is 4.61; see L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, 364 (1964).