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Electron Transfer. 25. Effectiveness of External Catalysts for Outer-Sphere Reactions[1]

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The activities of a variety of pyridine derivatives as catalysts for the Eu^{2+} and V^{2+} reductions of $(NH_3)_5pyCo^{3+}$ are compared. Data are interpreted in terms of sequence 1, in which the catalyst is reduced (k_1) to a radical intermediate, after which the intermediate may undergo reversal of the initial electron transfer (k_{-1}) or may react with Co(III) (k_2) in a rapid outer-sphere process. Several catalysts derived from 2,4-pyridinecarboxylic acid (I) are far more powerful than any reported previously. Although the specific rate k_1 is much more sensitive to catalyst structure than is the ratio k_2/k_{-1}, variation in the latter in this series is greater than has been observed in simple redox series that are unequivocally outer sphere. Moreover, k_1 values for the Eu^{2+} reductions are 10^2 to 10^3 times those for V^{2+}, in contrast to simple outer-sphere series in which V^{2+} is the more rapid reductant. The implication is that k_1 and k_{-1} refer to inner-sphere processes for the present group of catalysts. Cyclic voltammograms of all catalysts exhibit quasi-reversible reduction peaks (1 M $HClO_4$, 25 °C) in the range −0.53 to −0.81 V (vs. SCE). Conjugated species not exhibiting catalytic activity are reduced at potentials outside this range. It is suggested that the catalytic sequence is blocked if the potential barrier to reduction of the catalyst is too high but may become inoperative also in cases where the radical intermediate, although readily formed, is too sluggish a reductant.

Earlier communications reported that several 4-pyridinecarboxylato derivatives strongly catalyze outer-sphere reductions of Co(III) by Eu^{2+} and Cr^{2+} and presented evidence in support of the catalytic sequence

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

$$\mathrm{M} = \mathrm{Eu, Cr, V}$$

where "cat·" is a substituted pyridyl radical resulting from one-electron reduction of the catalyst.[2] A subsequent more detailed study,[3] in conjunction with pulse radiolytic data obtained in another laboratory,[4] allowed estimates of the rate constants for the individual steps associated with a variety of these catalyzed reactions. In general, catalytic effectiveness depends both on the rate at which the catalyst is reduced (k_1) and the competition between Co^{III} and M^{3+} (expressed as k_2/k_{-1}) for the radical intermediate, Cat·. Structural modification of the catalyst may result in considerable variation in k_1, but the ratio k_2/k_{-1} is much less sensitive, for any structural feature in the intermediate that facilitates its oxidation by Co(III) would be expected also to enhance its rate of oxidation by Eu^{3+}, Cr^{3+}, or V^{3+}. The reactivity patterns resulting from structural alteration of the oxidant are very much the same for catalyzed as for uncatalyzed reactions, but k_2 values associated with the catalyzed reductions of the more reactive Co(III) complexes appear to approach a maximum near, but not equal to, the diffusion-controlled limit.

In the present extension we have examined a number of additional catalysts, including some that are more powerful than any thus far encountered, and compared the action of several of these with Eu^{2+} and V^{2+} as reductants. We also describe experiments that indicate that catalytic effectiveness requires a species with a reduction potential lying in a relatively narrow range and that the initial reduction of the catalyst is, at least in some cases, an inner-sphere process.

Experimental Section

Materials. Solutions of europium(II),[5] vanadium(II),[6] and hexaammineruthenium(II)[7] were prepared by published procedures. Pyridinepentaamminecobalt(III) perchlorate, $(NH_3)_5pyCo(ClO_4)_3$, was prepared[8] and, when necessary for experiments involving Ru(II), converted to the corresponding trichloride[7] as described. Among the compounds examined for catalytic action, the 4-amide and 2,4-dimethyl ester of 2,4-pyridinedicarboxylic acid were prepared by the methods of Thunus,[9] N-methylated pyridine derivatives were prepared by the methylation procedure of Meyer,[10] *p*-methoxyphenylglyoxylic acid by the method of Businelli,[11a] trimethylpyruvic acid by the method of Rabjohn,[11b] and 2,4,6-pyridinetricarboxylic acid by the method of Tropsch.[11c] Other catalysts (Aldrich, Pfaltz and Bauer, or K&K products) were used as received.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[3,5a] Reductions with Eu^{2+} and V^{2+} were carried out under nitrogen, those with $Ru(NH_3)_6{}^{2+}$ under argon. No catalysis of the $Ru(NH_3)_6{}^{2+}$ reductions was observed, even when 2,4-pyridinedicarboxylic acid (the most powerful catalyst for the Eu^{2+} and V^{2+} reductions) was added in concentrations comparable to those of the substrates. Catalyzed reactions were first order each in reductant and catalyst. With reductant in excess, reactions catalyzed by species having donor oxygen atoms were first order in Co(III), whereas with other catalysts such as 4,4-bipyridyl, dependence on oxidant was more complex. Catalyzed reductions by Eu^{2+} were inhibited by added Eu^{3+}; those by V^{2+} were inhibited by V^{3+}. Rate measurements were generally made under pseudo-first-order conditions with either Co(III) or the reductant in greater than fivefold excess. Aside from reactions catalyzed by 2,4-pyridinedicarboxylic acid, rates were independent of acidity in the range 0.1–1.2 M H^+. Most measurements were carried out using 1.2 M $HClO_4$ as the supporting electrolyte. Reactions were followed for at least five half-lives, and rate constants were obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of kinetic runs.

Electrochemical Measurements. Cyclic voltammetric measurements were carried out using a PAR Model 137 potentiostat equipped with a Model 175 programmer. Voltammograms were recorded on a Houston Omnigraph recorder. The working electrode was a hanging mercury drop, the auxiliary electrode was a platinum plate, and the reference electrode was Hg/Hg_2Cl_2 in saturated KCl. The capillary from the salt bridge was placed very near to the working electrode. The supporting electrolyte was, in most cases, 1.0 M aqueous $HClO_4$, but a few measurements were made with 1.0 M $NaClO_4$. Distilled water used was boiled 30 min to remove dissolved oxygen, and prepurified nitrogen was slowly bubbled through the solution during measurements. No additional stirring was used. Potentials were varied between 0.0 and −1.2 V (vs. the SCE) beginning with the cathodic sweep. For runs in 1 M $HClO_4$, evolution of hydrogen dominated the voltammogram near the more negative limit. At a scan rate of 50 mV/s (that most generally used in our experiments) virtually all materials yielding a reduction peak also exhibited an oxidation peak, with the two half-peak potentials separated by 0.03–0.08 V. With pyrazine derivatives and quinoxaline, cathodic and anodic peaks were very nearly the same size; with pyridine derivatives and α-keto acids, the anodic peak was the smaller. In a few cases, scan rates were increased to 50 V/s, and the voltammogram was observed on an oscilloscope. Under such conditions the cathodic and anodic peaks again became nearly the same size, but the peak and half-peak potentials could no longer be satisfactorily estimated. Half-peak potentials varied by less 20 mV as sweep rates were increased from 20 to 100 mV/s.

Results and Discussion

Observed rates result from a combination of the catalyzed and uncatalyzed paths. Applying the steady-state approxi-

Table I. Kinetic Data for the Europium(II) Reduction of Pyridinepentaamminecobalt(III) as Catalyzed by 2,4-Pyridinedicarboxylic Acid

$10^3[\mathrm{Co^{III}}]$, M	$10^2[\mathrm{Eu^{2+}}]$, M	$10^6[\mathrm{Cat}]$, M	$10^2[\mathrm{Eu^{3+}}]$, M	$[\mathrm{H^+}]$, M	10^2k,[a] $\mathrm{s^{-1}}$
3.26	2.00	0	0	1.2	0.17
3.26	2.00	4.34	4.00	1.2	2.8
3.26	4.00	4.34	4.00	1.2	5.8
1.96	2.00	1.45	4.00	1.2	1.20
1.96	2.00	2.90	4.00	1.2	2.2
1.96	2.00	4.34	4.00	1.2	3.0
1.96	2.00	5.80	4.00	1.2	4.3
3.26	2.00	4.34	2.00	1.2	5.0
3.26	2.00	4.34	6.00	1.2	2.3
12.0	0.20	14.5	0	1.2	2.8
20.8	0.268	7.23	0	1.2	1.4
20.8	0.268	29.0	0	1.2	5.0
20.8	0.200	14.5	0	1.5	2.9
20.8	0.200	14.5	0	1.0	2.8
20.8	0.200	14.5	0	0.5	2.9
20.8	0.200	14.5	0	0.10	1.9
20.8	0.200	14.5	0	0.05	1.2
2.61	2.00	4.34	4.00	1.2	2.8
2.61	2.00	4.34	4.00	0.50	2.6
2.61	2.00	4.34	4.00	0.36	1.5

[a] Pseudo-first-order rate constants at 25 °C. Except for the reaction at 1.5 M $\mathrm{H^+}$, the sum $[\mathrm{HClO_4}] + [\mathrm{LiClO_4}]$ was maintained at 1.2 M.

Table II. Kinetic Data for the Vanadium(II) Reduction of Pyridinepentaamminecobalt(III) as Catalyzed by 2,4-Pyridinedicarboxylic Acid

$10^2[\mathrm{Co^{III}}]$, M	$10^3[\mathrm{V^{2+}}]$, M	$10^3[\mathrm{Cat}]$, M	$10^2[\mathrm{V^{3+}}]$, M	$[\mathrm{H^+}]$, M	10^2k,[a] $\mathrm{s^{-1}}$
2.00	1.87	0	0	1.2	0.60
2.00	1.87	0.875	0	1.2	1.90
2.00	1.87	1.75	0	1.2	3.9
2.00	1.87	2.63	0	1.2	5.8
2.00	2.00	4.81	0	1.2	8.7
2.00	2.00	7.22	0	1.2	14
2.00	2.00	9.62	0	1.2	17
2.00	2.00	1.67	0	1.43	3.5
2.00	2.00	1.67	0	0.54	3.9
2.00	2.00	1.67	0	0.25	4.6
2.00	2.00	1.67	0	0.15	5.3
2.00	2.00	1.67	0	0.072	5.3
2.00	2.00	1.67	0	0.052	5.3
1.00	1.87	1.75	0	1.2	4.1
0.210	40.0	0	0	1.2	1.5
0.210	20.0	0.833	4.0	1.2	5.0
0.210	20.0	0.500	4.0	1.2	2.8
0.210	40.0	0.500	4.0	1.2	5.3
0.210	20.0	0.833	2.7	1.2	6.3
0.210	20.0	0.833	5.3	1.2	3.2

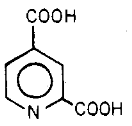
[a] Pseudo-first-order rate constants at 25 °C. Except for the reaction at 1.43 M $\mathrm{H^+}$, the sum $[\mathrm{HClO_4}] + [\mathrm{LiClO_4}]$ was maintained at 1.2 M.

mation to the radical intermediate, Cat· (which may be assumed to be present at much lower concentration than the oxidized form of the catalyst[12]), mechanism 1 leads to the rate law[2b,3]

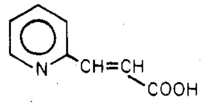
$$\text{rate} = \frac{k_1 k_2 [\mathrm{Co^{III}}][\mathrm{M^{2+}}][\mathrm{Cat}]}{k_{-1}[\mathrm{M^{3+}}] + k_2[\mathrm{Co^{III}}]} + k_{\mathrm{un}}[\mathrm{Co^{III}}][\mathrm{M^{2+}}] \qquad (2)$$

where the k_{un} terms refers to the uncatalyzed reaction. Observed first-order dependence on $\mathrm{M^{2+}}$, inhibition by $\mathrm{M^{3+}}$, and a first-order dependence on $\mathrm{Co^{III}}$ when $\mathrm{Eu^{2+}}$ is in large excess are in accord with this formulation. Moreover, when the uncatalyzed contribution is small, reactions are first order in catalyst, and when $\mathrm{Co^{III}}$ is in large excess, rates are very nearly zero order in oxidant. Under the latter conditions, $k_1[\mathrm{M^{2+}}][\mathrm{Cat}]$, representing initial electron transfer to the catalyst, becomes rate determining.

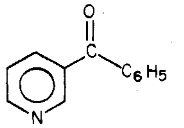
Kinetic data for typical systems, the $\mathrm{Eu^{2+}}$ and $\mathrm{V^{2+}}$ reductions of $\mathrm{Co(NH_3)_5py^{3+}}$, as catalyzed by 2,4-pyridinedicarboxylic acid (I), are presented in Tables I and II. For the europium reactions, when the initial concentrations of $\mathrm{Eu^{2+}}$ and $\mathrm{Eu^{3+}}$ are much greater than that of $\mathrm{Co^{III}}$, plots of the pseudo-first-order rate constants vs. the quotient $[\mathrm{Eu^{2+}}][\mathrm{Cat}]/[\mathrm{Eu^{3+}}]$ are linear with slope k_1k_2/k_{-1}. When $\mathrm{Co^{III}}$ is in excess, plots of rate constants vs. [Cat] are linear with slope k_1. A similar analysis applies to the vanadium reactions for which, however, the catalyst levels are 10^2 to 10^3 times as great as those with $\mathrm{Eu^{2+}}$. Values of k_1 and the ratio k_2/k_{-1} are summarized in Table III. Individual values of k_1 and k_2 cannot be obtained for these systems under steady-state conditions.



I



II



III

The structure of the Co(III) complex dictates an outer-sphere path for its reduction by the intermediate (the k_2 term), but there is no such restriction on the reduction of $\mathrm{Eu^{3+}}$ by Cat· (the k_{-1} term). If both k_2 and k_{-1} apply to outer-sphere processes, we would expect the ratio k_2/k_{-1} for the catalyzed $\mathrm{Eu^{2+}}$ reductions in this study to be independent of the identity of the catalyst (as would the corresponding ratio for the $\mathrm{V^{2+}}$ reductions), for the Marcus model predicts that the relative rates of outer-sphere oxidation of a given reductant by two or more oxidants should be the same for a series of reductants (and vice versa).[13]

Table III. Catalyzed Europium(II) and Vanadium(II) Reductions of Pyridinepentaamminecobalt(III). Kinetic Parameters

	Eu(II) reductions		V(II) reductions	
Catalyst	k_1[a]	k_2/k_{-1}	k_1[a]	k_2/k_{-1}
2,4-Pyridinedicarboxylic acid (I)	1.7×10^3	7.5	19	4.6
N-Methyl-2,4-pyridinedicarboxylic acid	1.5×10^3	22	12	7.9
2,4-Pyridinedicarboxylic acid dimethyl ester	1.6×10^3	14	6.5	22
2,4-Pyridinedicarboxylic acid 4-amide	1.6×10^3	2.5		
3,4-Pyridinedicarboxylic acid	1.6×10^3	4.3	1.9	2.7
2,6-Pyridinedicarboxylic acid	1.8×10^2	1.1		
2,4,6-Pyridinetricarboxylic acid	3.7×10^3		21	
2-Pyridylacrylic acid (II)	8.0	12		
N-Methyl-2-pyridinecarboxylic acid	*b*			
3-Benzoylpyridine (III)[d]	5.8			
4-Pyridylacrylic acid	28[c]	11[c]	0.1	6
4-Pyridinecarboxylic acid	14[c]	5.2[c]		
N-Methyl-4-pyridinecarboxylic acid	16[c]	7.1[c]		
Isonicotinamide	2.0[c]	7.6[c]		

[a] Values of k_1 (see mechanism 1 in text) are in $M^{-1}\ s^{-1}$. The ratio k_2/k_{-1} is dimensionless. Reaction temperatures were 25 °C. Reactions were carried out in 1.2 M $HClO_4$. [b] Marginal catalysis. [c] See ref 3. [d] Yellow-green pigment formed with Eu^{2+} in excess; kinetic studies were possible only with Co(III) in excess.

Table IV. Reduction Potentials, Estimated by Cyclic Voltammetry, for Electron-Transfer Catalysts and Noncatalysts in 1.0 M Aqueous $HClO_4$

Catalysts	E,[a] V	Noncatalysts	E,[a] V
4-Quinolineacrylic acid	−0.53	Quinoxaline	−0.11
N-Methyl-2,4-pyridinedicarboxylic acid	−0.55	Pyrazinetetracarboxylic acid	−0.16
		2-Quinoxalinecarboxylic acid	−0.17
3,4-Pyridinedicarboxylic acid	−0.58	Pyrazinecarboxylic acid	−0.23
2,4-Pyridinedicarboxylic acid 4-amide	−0.58	Pyrazinecarboxamide	−0.27
		Pyrazine	−0.29
1,2-Bis(4-pyridyl)ethylene	−0.62	Phenylglyoxylic acid	−0.34
2-Pyridylacrylic acid (II)	−0.62	4-Methoxyphenylglyoxylic acid	−0.38
Isonicotinamide	−0.65	2,4-Dimethoxyphenylglyoxylic acid	−0.38
2,4-Pyridinedicarboxylic acid (I)	−0.66	2,4,6-Trimethoxyphenylglyoxylic acid	−0.41
4-Pyridylacrylic acid	−0.70		
3-Benzoylpyridine (III)	−0.70	4-Benzoylpyridine	−0.38
Methyl viologen	−0.73	4-Acetylpyridine	−0.40
4,4′-Bipyridyl (diprotonated)	−0.75	Pyruvic acid	−0.63
N-Methyl-4-pyridinecarboxylic acid	−0.80	3-Pyridylacrylic acid	−0.91
4-Carbethoxypyridine	−0.81	Tropolone	−0.96
1,2-Bis(2-pyridyl)ethylene[b]	−0.64	Nicotinamide	−1.07
N-Methyl-2-pyridinecarboxylic acid[b]	−0.73	Di-2-pyridyl ketone	<−1.2
		4-Phenylpyridine	<−1.2

[a] Reduction potentials (vs. SCE, 23 °C) estimated as a mean of half-wave potential and peak potential for the first reduction wave. Sweep rate was 50 mV/s; reducible species were 10^{-3} M. [b] Marginal catalyst.

Although k_2/k_{-1} is found to be much less sensitive to catalyst structure than k_1, variation in this ratio is substantially greater than has been observed for relative rates in redox series where reactions are unequivocally outer sphere,[5a,7] thus indicating here a significant inner-sphere component to k_{-1} (and, by the principle of microscopic reversibility, a corresponding component in k_1).

This inference is strengthened by consideration of k_1 values. In those cases where catalyzed reductions by Eu^{2+} and V^{2+} are compared, k_1 for Eu^{2+} is seen to be 10^2 to 10^3 times that for V^{2+}. On the other hand, with bona fide outer-sphere oxidants, reductions by V^{2+} have been found, thus far without exception, to be more rapid than those by the lanthanide center.[7,14] This reversal in pattern may be taken as strong evidence that k_1 for Eu^{2+} in these reactions represents a process which is principally inner sphere but leaves in doubt the mechanism for V^{2+}. Although the observed k_1 values for V^{2+} (below 40 $M^{-1}\ s^{-1}$) are consistent with a path which is also predominantly inner sphere,[6a,15] they do not require this.[16,17]

Undoubtedly the most striking facet of the present work is the unusually great catalytic effectiveness of 2,4-pyridinedicarboxylic acid (I) and its derivatives. This augmented potency is seen to result from increases in k_1, the specific rate for reduction of the catalyst. Values of this parameter for the 2,4-disubstituted catalysts are 10^2 to 10^3 times those for the monosubstituted pyridines (the final four entries in Table III) which may be considered to be the prototype electron-transfer catalysts. The enhancement of catalysis does not appear to be primarily a thermodynamic effect, for the mono- and disubstituted catalysts are found (vide infra) to be reduced within the same range of potentials, nor, in general, can it be attributed to chelation,[18] for it persists when the ring nitrogen or the 2-COOH group of the catalyst is blocked off by methylation. Aside from these negative conclusions, however, we cannot, at this time, add anything useful.

A sufficient number of catalyst candidates, each capable of undergoing one-electron reduction, have now been examined to prompt the question, "is there any simple relationship between ease of reduction and catalytic effectiveness?" An answer would appear to be on firmest theoretical ground if standard potentials were compared, but such values have not been measured for all catalysts taken, and those available do not necessarily apply to aqueous solutions at high ionic strengths. In addition, most of the catalysts and the reduced radical intermediates they generate can exist both in protonated and a nonprotonated form;[19] the effective potential in a given solution will depend on the partition between protonated and nonprotonated species at both the oxidized and reduced levels and thus may be a complex function of acidity.

In seeking an approach which is both simple and convenient, we have carried out cyclic voltammetric measurements in media very closely related to those used in our kinetic experiments. A number of conjugated organic species examined in 1.0 M $HClO_4$ are listed in Table IV. Very nearly all exhibit at least one reduction and a corresponding oxidation peak, although there is some variation in the degree of reversibility throughout the series. All measurements are subject to junction potentials (one between the reference electrode and the salt bridge, the second between the bridge and primary electrolyte) which, however, are the same throughout. To put all compounds examined on a single scale, we have compared values of $^1/_2(E_{pc} + E_{pc/2})$, where the E values refer to the peak current potential and the half-peak potential for the first reduction wave. This mean is closely related to E^0 and is independent of sweep rate for reversible electrode reactions[20] (e.g., for reductions of pyrazine derivatives).[21] For reductions of substituted pyridines and α-keto acids,[22] values become perceptibly more cathodic at more rapid sweeps, but the shifts are not large enough to affect our conclusions.

Reduction potentials, thus estimated, have been found to lie between −0.53 and −0.81 V (vs. SCE) for all 17 compounds displaying catalytic activity in outer-sphere Eu^{2+}–Co(III) reactions. Of the 19 conjugated species found to be devoid of catalytic activity, 12 are reduced at potentials less negative than this range, whereas 6 require potentials which are more negative. The correlation is a reasonable one, for it may be argued that the catalytic sequence may be blocked if the potential barrier to the initial electron transfer is too high whereas it may become ineffective also if the radical intermediate is too sluggish a reductant.

Thirteen of the catalytically active compounds may be described as pyridine derivatives having an unsaturated function γ to the ring nitrogen. This is not, as was previously implied,[2a] a structural requirement for catalysis, for 2-pyridylacrylic acid (II), an α derivative, and 3-benzoylpyridine (III), a β derivative, both of which exhibit potentials in the range in question, are effective catalysts. The inactivity of pyruvic acid, the only acyclic species found to lie in this range, suggests the necessity of a nitrogen ring for catalysis of this sort, but additional nonheterocyclic molecules having appropriate potentials should be examined before this conclusion is firm.

The very approximate nature of the observed correlation scarcely needs reemphasis. Although all catalysts fall into a single range, there are no apparent subgroupings. Rather, within this range are scattered, at random, the most powerful catalysts, those of intermediate activity, and the marginal catalysts. This limitation is perhaps to be expected, for the differing degree of reversibility among the electroreductions (reflecting an unknown mix of absorption effects, autocatalytic processes, and secondary reactions of the radicals formed) results in a series of variable gaps between the recorded potentials and thermodynamic values. More important, even if the latter were available, they would relate only to the initial step (k_1) and its reversal (k_{-1}) for systems where these steps are uncomplicated by specific effects arising from bridging ligands and, moreover, could tell us nothing about variations in the partition ratio, k_2/k_{-1}, which governs the fate of the radical intermediate. The fact that even a rough relationship is observed indicates to us that despite these several complications acceptance of an electron by the catalyst, a step common to both the electroreductions and the catalyses, is of sufficient importance to set, in broad outline, the reactivity patterns associated with both types of process.

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Registry No. $(NH_3)_5pyCo^{3+}$, 31011-67-3; Eu(II), 16910-54-6; V(II), 15121-26-3; 2,4-pyridinedicarboxylic acid, 499-80-9; *N*-methyl-2,4-pyridinedicarboxylic acid, 62778-02-3; 2,4-pyridinedicarboxylic acid dimethyl ester, 25658-36-0; 2,4-pyridinedicarboxylic acid 4-amide, 24195-08-2; 3,4-pyridinedicarboxylic acid, 490-11-9; 2,6-pyridinedicarboxylic acid, 499-83-2; 2,4,6-pyridinetricarboxylic acid, 536-20-9; 2-pyridylacrylic acid, 7340-22-9; 4-pyridylacrylic acid, 5337-79-1; 4-quinolineacrylic acid, 13026-20-5; 1,2-bis(4-pyridyl)ethylene, 4916-57-8; isonicotinamide, 1453-82-3; 3-benzoylpyridine, 5424-19-1; methyl viologen, 1910-42-5; 4,4′-bipyridyl (diprotonated), 46040-54-4; *N*-methyl-4-pyridinecarboxylic acid, 824-77-1; 4-carbethoxypyridine, 1570-45-2; 1,2-bis(2-pyridyl)ethylene, 4916-40-9; *N*-methyl-2-pyridinecarboxylic acid, 445-30-7; quinoxaline, 91-19-0; pyrazinetetracarboxylic acid, 43193-60-8; 2-quinoxalinecarboxylic acid, 879-65-2; pyrazinecarboxylic acid, 98-97-5; pyrazinecarboxamide, 98-96-4; pyrazine, 290-37-9; phenylglyoxylic acid, 611-73-4; 4-methoxyphenylglyoxylic acid, 7099-91-4; 2,4-dimethoxyphenylglyoxylic acid, 26767-17-9; 2,4,6-trimethoxyphenylglyoxylic acid, 62778-01-2; 4-benzoylpyridine, 14548-46-0; 4-acetylpyridine, 1122-54-9; pyruvic acid, 127-17-3; 3-pyridylacrylic acid, 1126-74-5; tropolone, 533-75-5; nicotinamide, 98-92-0; di-2-pyridyl ketone, 19437-26-4; 4-phenylpyridine, 939-23-1.

References and Notes

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

(11) (a) M. Businelli, Italian Patent, 475964 (1952). *Chem. Abstr.*, **49**, 12539*d* (1955). This procedure, in which *p*-methoxyacetophenone is oxidized with alkaline $KMnO_4$, was adapted to the preparations of the 2,4-dimethoxy and 2,4,6-trimethoxy analogues. However, the recommended purification of the resulting keto acid through the $NaHSO_3$ addition compound was not applicable to the latter two syntheses. (b) N. Rabjohn and C. A. Harbert, *J. Org. Chem.*, **35**, 3727 (1970). (c) H. Tropsch, *Monatsh. Chem.*, **35**, 777 (1914).

(12) In the Eu^{2+} reduction of $(NH_3)_5pyCo^{3+}$ as catalyzed by isonicotinamide, for which values of k_1, k_{-1}, and k_2 have been determined,[3] the ratio [Cat·]/[Cat] may be calculated to be 5×10^{-8} when $[Eu^{2+}] = 0.002$, $[Eu^{3+}] = 0.001$, and $[Co^{III}] = 0.02$ M. This ratio increases to 1.5×10^{-6} when $[Eu^{2+}] = 0.02$, $[Eu^{3+}] = 0.04$, and $[Co^{III}] = 0.002$ M.

(13) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964). In the present case, the reductants being compared are the various radical intermediates [Cat·]. An earlier study[3] has shown these intermediates to conform to the Marcus picture.

(14) The ratio of specific rates, $k_V/k_{Eu} = 3$, shown by Fan[7] to apply to uncatalyzed outer-sphere reactions between metal centers, has been recently found (Y.-T. F., Kent State University, 1976) to be appropriate also for the initial step in catalyzed reactions when the absence of a lead-in group on the catalyst ensures that this step is outer sphere.

(15) (a) B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967); (b) J. C. Chen and E. S. Gould, *ibid.*, **95**, 5539 (1973).

(16) The ineffectiveness of our catalysts for reductions by $Ru(NH_3)_6{}^{2+}$, an outer-sphere reducing agent, also hints that formation of the intermediate is an inner-sphere process. However, the relatively low potential of this reductant ($E^0 = +0.214$ V)[17] dictates caution in drawing this inference.

(17) J. F. Endicott and H. Taube, *Inorg. Chem.*, 4, 437 (1965).

(18) Chelation may play a minor role, however, in the V^{2+} reduction as catalyzed by 2,4-pyridinedicarboxylic acid, which is seen (Table II) to be somewhat more rapid at 0.052 M than at 0.54 M H^+. This difference may reflect a slight increase in the association constant for the V(II)-catalyst precursor complex resulting from deprotonation of the catalyst (in part) at 2-COOH.

(19) See, for example, (a) U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974); (b) P. N. Moorthy and E. Hayon, *J. Phys. Chem.*, **78**, 2615 (1974).

(20) See, for example, A. F. Fry "Synthetic Organic Electrochemistry", Harper and Row, New York, N.Y. 1972, p 83.

(21) L. N. Klatt and R. L. Rouseff, *J. Am. Chem. Soc.*, **94**, 7295 (1972).

(22) One-electron reductions of α-keto acids have been described, for example, by T. Fujisawa, B. M. Monroe, and G. S. Hammond, *J. Am. Chem. Soc.*, **92**, 542 (1970).