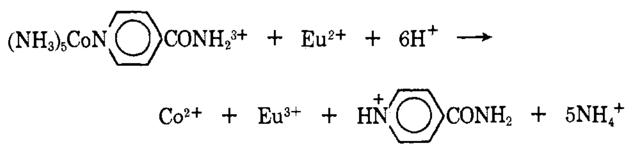
Radical-Catalyzed Electron Transfer

Sir:

The participation of organic radicals in metal-ion electron-transfer reactions has been proposed on the basis of previous studies[1-4] in which the organic molecules acted as bridging groups. We now present striking evidence that organic molecules can provide a facile reaction pathway for electron transfer by virtue of their ability to form radicals.

We have studied the reaction



by following the change in absorbance at the isonicotinamidepentaamminecobalt(III) maximum at 474 nm as a function of time. Typical absorbance traces are shown in Figures 1 and 2. The absorbance changes deviate markedly from those expected for a reaction first order in both cobalt(III) and Eu^{2+}. The rate of the reaction does not diminish as expected for a second-order reaction, and in some experiments the reaction rate remains almost constant through a large part of the reaction.

Separate experiments in which Co^{2+} and NH_4^+ were added to the initial reaction mixture showed that these ions had no effect on the progress of the reaction. However, free isonicotinamide accelerated the reaction rate, whereas Eu^{3+} ion (see Figure 2) mildly inhibited the reaction rate. The following mechanism is in agreement with these observations

$$H^+ + Co^{III}L + Eu^{2+} \xrightarrow{k_1} Co^{2+} + Eu^{3+} + HL^+ \qquad (1)$$

$$HL^+ + Eu^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HL\cdot + Eu^{3+} \qquad (2)$$

$$H^+ + HL\cdot + Co^{III}L \xrightarrow{k_3} Co^{2+} + 2HL^+ \qquad (3)$$

where ammonia has been omitted for clarity and L = isonicotinamide.

The Eu^{2+} reductions of the pyridine- and nicotinamidepentaamminecobalt(III) complexes do not exhibit autocatalysis but instead show the usual second-order behavior. Furthermore, the reductions of both the pyridine and nicotinamide complexes are catalyzed by free isonicotinamide. The sensitivity of Eu^{2+}–Co^{III} reactions to catalysis was previously noted by Doyle and Sykes,[5] who suggested the participation of radicals in the main reaction. Recent experiments of Gould and coworkers have also shown that organic molecules catalyze Eu^{2+} reductions.[6] A mechanism analogous to the one above can be written for the isonicotinamide-catalyzed reductions of the pyridine complex

$$H^+ + Co^{III}py + Eu^{2+} \xrightarrow{k_1'} Co^{2+} + Eu^{3+} + Hpy^+ \qquad (4)$$

$$HL^+ + Eu^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HL\cdot + Eu^{3+} \qquad (2)$$

$$H^+ + HL\cdot + Co^{III}py \xrightarrow{k_3'} Co^{2+} + HL^+ + Hpy^+ \qquad (5)$$

where ammonia has been omitted for clarity and L = isonicotinamide.

Oxidation potentials of 0.43 V for the $Eu^{2+|3+}$ couple[7] and ~0.9 V for the $HL\cdot|HL^+$ couple[8] indicate that the equilibrium for reaction step 2 lies far to the left and the concentration of $HL\cdot$ is always small. We make the steady-state assumption for $HL\cdot$ and obtain the following rate law

$$-\frac{d[Co^{III}]}{dt} = k_1[Co^{III}][Eu^{2+}] + \frac{k_2k_3[Co^{III}][Eu^{2+}][HL^+]}{k_{-2}[Eu^{3+}] + k_3[Co^{III}]} \qquad (6)$$

This rate law applies to both of the above mechanisms, but takes on its simplest form in the latter case where $[HL^+]$ is constant during the reaction (and k_1' and k_3' replace k_1 and k_3 in the expression). In kinetic runs with large $[Co^{III}]$, where $k_3[Co^{III}] \gg k_{-2}[Eu^{3+}]$ and the $[Co^{III}]$ is essentially constant throughout the reaction, the observed second-order rate constant, k_{obsd}, is given by

$$k_{obsd} = k_1' + k_2[HL^+][Co^{III}]^{-1}$$

This rate expression was tested in runs with $[H^+] = 0.9\ M$, $[HL^+] = 0\text{–}6 \times 10^{-3}\ M$, $[Eu^{2+}] = 0.84 \times 10^{-3}\text{–}1.56 \times 10^{-3}\ M$, and $[(NH_3)_5Co^{III}py]_0 = 9.33 \times 10^{-3}\text{–}37.3 \times 10^{-3}\ M$. Plots of k_{obsd} *vs.* $[HL^+]$ at fixed $[Co^{III}]$ and of k_{obsd} *vs.* $[Co^{III}]^{-1}$ at fixed $[HL^+]$ were linear within experimental error. A least-squares analysis gave $k_1' = 0.07 \pm 0.03\ M^{-1}\ sec^{-1}$ and $k_2 = 1.8 \pm 0.1\ M^{-1}\ sec^{-1}$ at 25° and 1.0 *M* ionic strength.

The Eu^{2+} reductions of the isonicotinamide complex were studied at 25° and 1.0 *M* ionic strength in the ranges $[H^+]_0 = 0.07\text{–}0.97\ M$, $[Co^{III}]_0 = 1 \times 10^{-3}\text{–}4 \times 10^{-3}\ M$, and $[Eu^{2+}] = 1.38 \times 10^{-3}\text{–}2.0 \times 10^{-3}\ M$. In every case, autocatalytic behavior was observed and therefore special ways of treating these data were devised.

The specific rate for the noncatalytic reduction was estimated from the initial slope of second-order kinetic plots. The value of $k_1 = 0.83 \pm 0.20\ M^{-1}\ sec^{-1}$[8a] was found for the isonicotinamide complex. Within

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[1] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

[2] F. Nordmeyer and H. Taube, *ibid.*, **90**, 1162 (1968).

[3] H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

[4] M. V. Olson and H. Taube, *ibid.*, **9**, 2072 (1970).

[5] J. Doyle and A. G. Sykes, *J. Chem. Soc. A*, 2836 (1968).

[6] J. R. Barber, Jr., and E. S. Gould, *J. Amer. Chem. Soc.*, **93**, 4045 (1971). We thank Professor Edwin S. Gould for communicating his results prior to publication.

[7] W. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952.

[8] W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Amer. Chem. Soc.*, **83**, 3164 (1961), report a half-wave potential of −1.06 V for *N*-ethylisonicotinamide in acetonitrile media. The potential could not be measured in water. However, the half-wave potential of *N*-ethyl-4-cyanopyridine is −0.79 V in acetonitrile and is −0.87 V in aqueous media. A half-wave potential of −1.14 V (*vs.* sce) could be estimated for *N*-ethylisonicotinamide in water which corresponds to an oxidation potential of 0.89 V for the $EtL\cdot|EtL^+$ couple. The $HL\cdot|HL^+$ couple should have a similar potential.

[8a] NOTE ADDED IN PROOF. More sensitive experiments to determine k_1 are in progress.

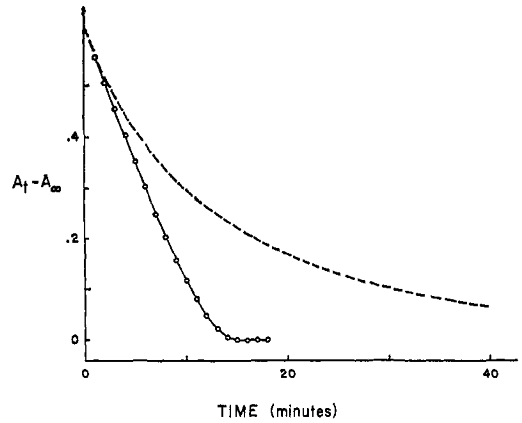

Figure 1. Absorbance change accompanying Co^{III} reduction: (—) observed for a reaction at 25° and 1.0 M ionic strength, where $[Co^{III}]_0 = 1.0 \times 10^{-3}$ M, $[Eu^{2+}]_0 = 2 \times 10^{-3}$ M, and $[H^+]_0 = 0.97$ M; (- - -) calculated for the same reaction according to the rate law $-d[Co^{III}]/dt = 0.83$ M^{-1} sec^{-1} $[Co^{III}][Eu^{2+}]$.

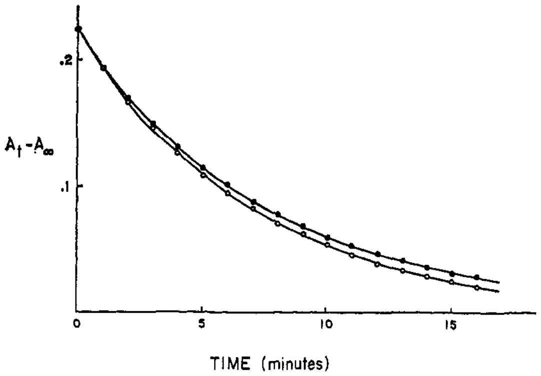

Figure 2. Eu^{3+} dependence of Co^{III} reduction. Reactions are at 25° and 1.0 M ionic strength, where $[Co^{III}]_0 = 2.0 \times 10^{-3}$ M, $[Eu^{2+}]_0 = 3.6 \times 10^{-4}$ M, and $[H^+]_0 = 0.88$ M: (○) no initial Eu^{3+}, (●) $[Eu^{3+}]_0 = 0.021$ M.

experimental error, this value was independent of $[H^+]$, $[Co^{III}]$, and $[Eu^{2+}]$.

In order to verify the form of the rate law for the isonicotinamide complex, rate eq 6 was integrated and used as the basis of a nonlinear least-squares program.[9] The program calculated the optimum value of each of the three independent parameters, k_1, k_2, and k_{-2}/k_3, which reproduce the absorbance–time data for each run. For the experiments involving the isonicotinamide complex, values ranged from 0.7 to 1.3 M^{-1} sec^{-1} for k_1, from 1.0 to 2.5 M^{-1} sec^{-1} for k_2, and from 0.01 to 0.07 for k_{-2}/k_3. In every case, satisfactory fits to the absorbance–time data were obtained.

Rate law 4 is consistent with the autocatalytic data obtained. There is, however, a great deal of uncertainty in the parameters. We observed in the course of these studies that the most marked deviations occurred in runs in which the $(Co^{III})/(Eu^{2+})$ ratio was low. Apparently some HL· may be lost to further reduction by Eu^{2+}. Our observation that free isonicotinamide is rapidly reduced by Eu^{2+} lends support to this suggestion.

Better values of k_1 and k_{-2}/k_3 can be obtained from the data by fixing the value of k_2 at 1.8 M^{-1} sec^{-1}, a value known from the previous experiments. With k_2 fixed at 1.8 M^{-1} sec^{-1}, values of $k_1 = 0.85 \pm 0.15$ M^{-1} sec^{-1} and $k_{-2}/k_3 = 0.011$–0.027 are found. The value of k_1 is in excellent agreement with that obtained from the initial slope of the second-order plots.

The reactions studied in this communication provide direct evidence for a radical-catalyzed electron-transfer mechanism. These observations also support the radical-intermediate mechanism for bridging ligands as proposed for Cr^{2+} reductions.[1] The rate of electron transfer to isonicotinamide will not be greatly affected by replacing H$^+$ with $(NH_3)_5Co^{III}$ since neither interacts with the π-acceptor orbitals of the aromatic ring. Thus, if electron transfer to the bridging ligand is the primary activation process for Co^{III} reduction, then the rate of Co^{III} reduction will be similar to and cannot greatly exceed the rate of electron transfer to the ligand.

Such is the case in the present Eu^{2+} reductions. The similarity of the specific rate of Co^{III} reduction, 0.83 M^{-1} sec^{-1}, to the specific rate of electron transfer to HL$^+$, 1.8 M^{-1} sec^{-1}, indicates that isonicotinamide may act as a bridging ligand according to a radical-intermediate mechanism. This conclusion was reached for the Cr^{2+} reduction of complexes of this bridging ligand.[2] The similarity between Cr^{2+} and Eu^{2+}[10] is reasonable, since they have similar oxidation potentials and also share a tendency to exhibit inner-sphere paths.

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(9) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963); IBM Share Program, SDA No. 3094, 1964.

(10) In spite of the similarity, an autocatalytic path is not observed for the corresponding Cr^{2+} reduction. The reason for this probably stems from the substitution-inert character of Cr^{III}. The analogous reaction for Cr^{2+} would be

$$Cr^{2+} + HL^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HL\cdot Cr^{III}$$

$$Co^{III} + HL\cdot Cr^{III} \xrightarrow{k_3} Co^{2+} + HLCr^{III}$$

Since Cr^{III} remains attached to HL·, return of the electron to Cr^{III} in a unimolecular decomposition would predominate over product formation by electron transfer to Co^{III} *via* a bimolecular process.

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Electron Transfer through Organic Structural Units. X. Catalysis, by Pyridine Derivatives, of Outer-Sphere Reductions of Cobalt(III). Evidence for an Unusually Reactive Outer-Sphere Reducing Agent

Sir:

The outer-sphere reductions, by Cr^{2+} or Eu^{2+}, of such slowly reacting oxidants as $(NH_3)_6Co^{3+}$, $(NH_3)_5$-$pyCo^{3+}$, and $(NH_3)_5(DMF)Co^{3+}$ are dramatically accelerated by certain pyridine derivatives having a carbonyl or alkenyl substituent γ to nitrogen. Among catalysts acting in this manner are 4-pyridinecarboxylic acid, its carboxyl-bound $(H_2O)_5Cr^{III}$ derivative, and 1,2-bis(4-pyridyl)ethylene. The corresponding α derivatives have marginal catalytic action, and the β derivatives none. No such catalysis was observed with pyridine, 3-pyridinesulfonic acid, 4-cyanopyridine, 1,2-bis(4-pyridyl)ethane, or p-aminobenzoic acid. N-Alkylation of the pyridinecarboxylato catalysts enhances activity.