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

Electron Transfer. 39. Catalyzed Reductions of Cobalt(III) by Uranium(III)[1]

MARILYN K. LOAR, Y.-T. FANCHIANG, and EDWIN S. GOULD*

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The reduction of $Co(en)_3^{3+}$ with U^{3+} is strongly catalyzed by uncoördinated pyridine derivatives of the type known to catalyze the outer-sphere reductions of Co(III) complexes by Eu^{2+} and V^{2+}. Catalysis is inhibited by U^{4+}. As with the dipositive reductants, kinetic data are interpreted in terms of a sequence in which the catalyst is first reduced (k_1) to a radical intermediate, which may then undergo reversal of the initial step (k_{-1}) or may react with $Co(en)_3^{3+}$ (k_2). The present results, in conjunction with earlier data,[2] allow us to estimate k_1, k_{-1}, and k_2 for reactions catalyzed by isonicotinamide, nicotinamide, and methylviologen. Values of the composite specific rate k_1k_2/k_{-1} are in agreement with those calculated using the formal potentials of U^{3+} and the catalysts and a linear free energy relationship (eq 3 in the text) which links k_2 to $E°_{Cat}$. The ratio k_{-1}/k_2 lies near 1/3 for nicotinamide and isonicotinamide but is 1/700 for methylviologen, which can participate only in outer-sphere processes. This difference points strongly to an inner-sphere path for the k_{-1} step involving the two amides and, by implication, for the initial reduction (k_1) as well. The high specific rates (10^4–10^6 M^{-1} s^{-1}) for these inner-sphere acts indicate that ligand substitutions about the U(III) and U(IV) centers are rapid. The k_1 value for the reaction catalyzed by methylviologen, in combination with the Marcus treatment,[11] allows us to estimate a self-exchange rate of 5×10^{-2} M^{-1} s^{-1} (25 °C, $\mu = 1.0$) for U^{3+}–U^{4+}.

In previous studies dealing with the outer-sphere reductions of cobalt(III), as catalyzed externally by pyridine derivatives which themselves undergo reversible one-electron reductions, the most straightforward kinetic picture was obtained when europium(II) or vanadium(II) was taken as the reducing center.[2] Although a substantial body of evidence was gathered in support of catalytic sequence 1, it was recognized that

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

several features could introduce complications in these or in analogous systems. The observed[2a,3] deterioration of catalyst function with use may be attributed to the gradual destruction of the catalyst by a combination of bimolecular termination acts and slow reduction of the radical intermediate, Cat·, to an inactive two-electron product; this attrition would be expected to be most troublesome with the most powerful reducing centers. A second point concerns the degree of reversibility of the initial step, particularly when this is an inner-sphere process. In Cr^{II}–Cr^{III} systems, for example, the slow substitution about the Cr^{III} center curtails reversibility so that inhibition of the catalytic path by M^{3+}, which is quite characteristic of Eu(II) and V(II) reductions, is not observed.[2d]

The present extension of our catalytic studies to the very strongly reducing species U^{3+} ($E° = -0.63$ V)[4] relates to these matters. We were interested particularly in what could be learned about the ease of ligand substitution about the uranium(IV) center, a question on which direct evidence is lacking.

Experimental Section

Materials. Tris(ethylenediamine)cobalt(III) chloride, $Co(en)_3Cl_3$, was prepared as described[5] and converted to the corresponding perchlorate by dissolving in warm water and adding an equal volume of 70% $HClO_4$. The solution and precipitation steps were repeated until the product gave a negative chloride test. Since this complex was used in large excess in most of our kinetics experiments, it was essential that it be free of impurities reducible by U^{3+}. Uranium(III) perchlorate solutions were prepared as described.[6] Uranium(IV) solutions were prepared by bubbling air through acidic U(III) solutions for 15 min. Thorium perchlorate (Alfa) and catalysts (Aldrich) were used as received.

Rate Measurements. Rates were estimated by following absorbance decreases on the Cary 14 recording spectrophotometer as described.[2a,6] All experiments involved $Co(en)_3^{3+}$, which, in the absence of catalysis, is one of the most sluggish Co(III) oxidants known. Measurements were made at 350 nm (where absorption by U^{3+} is dominant).[7] Reactions were carried out under nitrogen. The supporting medium was generally 0.25 M in $HClO_4$ with the ionic strength adjusted to 0.50 M with $LiClO_4$. Reductions were first order in U^{3+} but exhibited a more complex dependence (see below) on $[Co^{III}]$. Experimental runs were generally made under pseudo-first-order conditions with the ratio $[Co^{III}]/[U^{3+}]$ greater than 10. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run generally agreed to within 5%. No trends indicative of systematic errors within a single run were noted, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 8%, except for those reactions catalyzed by isonicotinic acid, which showed somewhat greater scatter. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Deterioration of catalyst function with use, as described in earlier reports,[2a,3] was more serious for U^{3+} than for Eu^{2+} or V^{2+}, although experimental conditions were chosen to minimize this difficulty. Successive runs with the same sample of catalyst were characterized by apparent rate constants which decreased by 10–15% for each charge of U^{3+}.

Stoichiometry. Stoichiometry experiments, in which solutions of properly purified $Co(en)_3(ClO_4)_3$ and catalyst in 0.25 M $HClO_4$ were treated with a measured, deficient quantity of U^{3+}, were carried out in a manner similar to that described.[8] After these mixtures were allowed to react for 10 min, the quantity of Co^{2+} formed was estimated

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as described.[8b] In cases where the catalyst/Co(III) ratios corresponded to those employed in the kinetic runs, 0.96–0.99 mol of Co^{2+} were formed for each 1 mol of U^{3+} taken. At higher ratios, yields of Co^{2+} were less, with departures from 1/1 stoichiometry most marked at the highest catalyst concentrations, indicating a progressively increasing degree of consumption of U^{3+} by the catalyst.

Results and Discussion

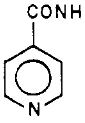
Although application of the steady-state approximation to the intermediate, "Cat·", in sequence 1, leads, as in earlier work,[2] to rate law 2, the present system differs from those in

$$\text{rate} = \frac{k_1k_2[\mathrm{Co^{III}}][\mathrm{U^{3+}}][\mathrm{Cat}]}{k_{-1}[\mathrm{U^{4+}}] + k_2[\mathrm{Co^{III}}]} + k_{\mathrm{un}}[\mathrm{Co^{III}}][\mathrm{U^{3+}}] \quad (2)$$

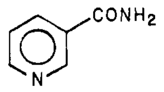
most previous studies in that the k_{un} term, which pertains to the uncatalyzed reaction, cannot be ignored. Moreover, since we could not carry out kinetic runs with U^{3+} in excess,[7] we were unable to extend our study to concentration regions where the reaction is very nearly first order in $Co(en)_3^{3+}$. In accord with (2), however, the composite reaction was found to be first order in U^{3+} in all cases.

Representative kinetic data for the reduction, as catalyzed by isonicotinamide, I, appear in Table I. Note that the reaction is inhibited by addition of U^{4+}, reflecting the reversibility of the initial step in sequence 1, but not by comparable concentrations of Th^{4+} (a 4+ ion having nearly the same size as U^{4+} but being incapable of undergoing a one-electron reduction). In the absence of added U^{4+}, the initial term in (2) simplifies to $k_1[\mathrm{U^{3+}}][\mathrm{Cat}]$. Under these conditions, and with [Co(III)] held constant, plots of pseudo-first-order rate constants (i.e., values of rate/$[\mathrm{U^{3+}}]$) vs. [Cat], which are closely linear, yield k_1 as slope and k_{un}[Co(III)] as intercept.[9]

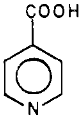
For reactions in the presence of added U^{4+}, with [Co(III)] and [Cat] held constant, plots of $1/k_{\mathrm{Cat}}$ (where k_{Cat} is the observed pseudo-first-order rate constant adjusted for the small uncatalyzed component) vs. $[\mathrm{U^{4+}}]$ are also linear with a slope equal to $k_{-1}/k_1k_2[\mathrm{Co(III)}][\mathrm{Cat}]$ and an intercept $(k_1[\mathrm{Cat}])^{-1}$.



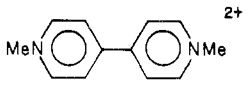
I



II



III



IV

Kinetic parameters thus calculated for reactions catalyzed by isonicotinamide, I, are listed in Table II, together with parameters obtained in an analogous manner for the remaining catalysts. Note that the k_1 values derived from variation of [Cat] are in good agreement with those obtained by variation in $[\mathrm{U^{4+}}]$.

The structure of the oxidant dictates an outer-sphere path for reaction of the intermediate, Cat·, with $Co(en)_3^{3+}$ (the k_2 step) in all cases. Moreover, the absence of lead-in substituents on methylviologen, IV, ensures that the initial reduction of this catalyst and its reversal are outer-sphere processes as well. For the outer catalysts, which feature –COOH or –$CONH_2$ groups, there is evidence that a bridged path intervenes in the reactions with U^{3+} and in the reverse reactions, which involve U^{4+}.

It has been shown[2a,c,10] that values of k_1, the specific rates at which a series of catalysts react with a given reductant, depend both on reduction potentials and on the availability of an inner-sphere path for electron transfer. Thus, the much greater k_1 for isonicotinamide ($E° = -0.66$ V)[10] than for nicotinamide ($E° = -0.96$ V)[10] reflects mainly the difference in the potentials of the two catalysts. On the other hand, our observation that methylviologen ($E° = -0.52$ V)[2c] and isonicotinamide, despite the marked difference in their potentials, exhibit similar specific rates hints that an additional path not available to the dication is being used in reduction of the amide.

Table I. Kinetic Data for the Uranium(III) Reduction of Tris(ethylenediamine)cobalt(III), $Co(en)_3^{3+}$, As Catalyzed by Isonicotinamide

10^2[Co(III)], M	10^5[Cat], M	$10^2[\mathrm{U^{4+}}]$, M	10^2k,[a] s^{-1}
0	2.4	0	0.007
1.03	0	0	0.33
1.03	0.296	0	1.0
1.03	0.592	0	1.6
1.03	0.888	0	2.4
1.03	1.18	0	2.9
1.03	1.78	0	4.3
1.03	2.36	0	5.0
0.42	1.18	0	2.6
2.06	1.18	0	4.2
0.42	2.34	1.22	2.2
2.06	2.34	1.22	3.5
1.02	2.40	0	5.0[b]
1.02	2.40	0.246	4.9
1.02	2.40	0.491	4.2
1.02	2.40	0.918	4.0
1.02	2.40	1.77	3.1

[a] Pseudo-first-order specific rates at 25 °C. Reaction medium was 0.25 M $HClO_4$ with μ adjusted to 0.50 M with $LiClO_4$. $[\mathrm{U^{3+}}]_0$ was 1.17×10^{-4} M throughout. Disappearance of U^{3+} was monitored at 350 nm. [b] Reaction mixture was 0.018 M in $Th(ClO_4)_4$.

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

catalyst	k_1	k_1k_2/k_{-1}	k_2	k_{-1}
isonicotinamide, I	2.0×10^3 [b] 2.2×10^3 [c]	5.9×10^3 [c]	3×10^4 [d]	1×10^4
nicotinamide, II	4.2[b] 4.4[c]	15.4[c]	3×10^6 [e]	8×10^5
isonicotinic acid, III	2.1×10^4 [b] 2.0×10^4 [c]	9.8×10^3 [c]		
methylviologen, IV	4.6×10^3 [b]		5×10^4 [f]	70[g]

[a] Values of k_1, k_{-1}, and k_2 (see sequence 1) are in $M^{-1}\ s^{-1}$. Reaction temperatures were 25 °C. Reactions were generally carried out in 0.25 M $HClO_4$ with μ adjusted to 0.50 M with $LiClO_4$. [b] Determined by variation in [catalyst] (see text). [c] Determined by variations in added U^{4+}. [d] See ref 2a. [e] See ref 10. [f] See ref 2c. [g] Calculated from the Nernstian dependence of k_1/k_{-1} on the standard potentials of catalyst and U^{3+}.

This inference is strongly reinforced by consideration of the k_{-1} values. If reaction of U^{4+} with the radical Cat· were outer sphere throughout, the ratio k_{-1}/k_2 would be expected to be nearly the same for all catalysts, for the Marcus model predicts that the relative rates of outer-sphere oxidation of a given reductant by two oxidants should be the same for a series of reductants.[11] However, this ratio lies near 1/3 for the two amides but is 1/700 for methylviologen. Hence, we may conclude that U^{4+} oxidation of the amide radicals proceeds principally by an inner-sphere path which is denied to the radical from methylviologen. Microscopic reversibility then requires that the corresponding distinction in mechanism apply also to the forward (k_1) step.

Note also that the high k_1 values found for isonicotinic acid and its amide and the high k_{-1} values for the two catalytic amides, in conjunction with the assignment of an inner-sphere path to the steps involved, imply that ligand substitution about the U(III) and U(IV) centers, which must precede any act of inner-sphere electron transfer, is rapid. This conclusion occasions no astonishment in the case of U(III), which has been shown[12] to reduce appropriately substituted Co(III) complexes (almost certainly via the inner-sphere path) at specific rates exceeding $10^5\ M^{-1}\ s^{-1}$ at 25 °C. However, the

Table III. Comparison of Calculated and Observed Composite Rate Constants for Catalyzed Reductions of $Co(en)_3^{3+}$ by U^{3+}

	$\log (k_1k_2/k_{-1})$	
catalyst	exptl[a]	calcd[b]
isonicotinamide, I	3.77	3.71
nicotinamide, II	1.19	1.16
isonicotinic acid, III	3.99	3.71[c]
methylviologen, IV	6.52	6.33

[a] Specific rates (25 °C, $\mu = 0.50$), defined in sequence 1. [b] Calculated using eq 3 (see ref 10). Parameters applying to reactions in 1 M $HClO_4$ were taken without adjustment. [c] Calculated by assuming the standard potential of isonicotinic acid to be the same as that for isonicotinamide.

substitution lability of U(IV) does not appear to have been demonstrated previously.

Equation 3 has recently been proposed[10] as a relationship

$$\log \left[\frac{k_1k_2}{k_{-1}}\right] = (E°_{\text{Cat}} - E°_{\text{Red}})\frac{F}{2.3RT} + 3.81 - 5.17E°_{\text{Cat}} + \log \left[\frac{k_{\text{Ox}}}{k_{\text{Co(py)}}}\right]_{\text{un}} \quad (3)$$

between the composite specific rate k_1k_2/k_{-1} for catalytic systems analogous to these and the formal potentials of the reductant ($E°_{\text{Red}}$) and catalyst ($E°_{\text{Cat}}$). Here the final term includes the ratio of specific rates, using a common reductant, for the uncatalyzed reductions of the oxidant at hand and for $(NH_3)_5Co(py)^{3+}$, which has been taken as a standard. Substitution of appropriate $E°$ values and known[6] specific rates for the uncatalyzed reductions of $Co(en)_3^{3+}$ and $(NH_3)_5Co(py)^{3+}$ yields calculated values of k_1k_2/k_{-1}, which are seen (Table III) to be in reasonable agreement with experiment.

Finally, we may use k_1 for the reaction catalyzed by methylviologen, IV, to estimate the specific rate for self-exchange in the system U^{3+}–U^{4+}. For the U^{3+}–methylviologen reaction, which features a moderate difference in formal potentials (0.14 V), Marcus's treatment[11] yields the approximate relationship

$$k_{\text{U,MV}} = (k_{\text{MV}}^{\text{ex}} k_{\text{U(3,4)}} K_{\text{U,MV}})^{1/2} \quad (4)$$

where $k_{\text{MV}}^{\text{ex}}$ is the specific rate for self-exchange in the MV–MV· system, $k_{\text{U(3,4)}}$ is that in the U^{3+}–U^{4+} system, and $K_{\text{U,MV}}$ is the equilibrium constant for the reaction. Combining this with a similar cross relation applied to the V^{2+}–methylviologen reaction ($k = 2.3\ M^{-1}\ s^{-1}$ at 25 °C and $\mu = 1$)[2c] leads to eq 5, which includes neither the self-exchange rate

$$\log \left[\frac{k_{\text{U,MV}}}{k_{\text{V,MV}}}\right] = \frac{1}{2} \log \left[\frac{k_{\text{U(3,4)}}}{k_{\text{V(2,3)}}}\right] - \frac{1}{2}\left[\frac{E°_{\text{U}} - E°_{\text{V}}}{0.059}\right] \quad (5)$$

of the catalyst nor its formal potential. The value of $k_{\text{U,MV}}$ at unit ionic strength may be taken as $10^4\ M^{-1}\ s^{-1}$, i.e., about twice its value at $\mu = 0.5$.[13,14] Substitution of the reported[15] self-exchange rate for V^{2+}–V^{3+} ($0.01\ M^{-1}\ s^{-1}$) and the standard potentials for U^{3+} (−0.63 V)[4] and V^{2+} (−0.24 V)[16] then allows us to calculate $k_{\text{U(3,4)}}$ to be $0.05\ M^{-1}\ s^{-1}$ at 25 °C and $\mu = 1$, a value remarkably close to that for $k_{\text{V(2,3)}}$ but over 10^2 as great as the rate in the Eu^{2+}–Eu^{3+} system,[17,18] which also involves transfer of an f electron. To the extent that this calculation is credible,[18] it implies that the kinetic advantage that U^{3+} enjoys over V^{2+} in the reaction with methylviologen is derived almost wholly from its more favorable potential, rather than from the ease with which it undergoes self-exchange.

Registry No. $Co(en)_3^{3+}$, 14878-41-2; U^{3+}, 22578-81-0; I, 1453-82-3; II, 98-92-0; III, 55-22-1; IV, 4685-14-7.

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