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

Electron Transfer. 34. A Relationship between Catalytic Effectiveness and Reduction Potential[1]

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

Received October 21, 1977

Kinetic data are presented pertaining to the action of additional catalysts which accelerate the outer-sphere reactions of $Co(NH_3)_5py^{3+}$ with reducing metal ions and operate via the sequence

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

This extension more than doubles the range of formal reduction potentials ($E°_{Cat}$) associated with catalysts having known kinetic parameters for sequences of this type. Values of k_2 conform to the relationship $\log k_2 = 3.81 - 5.17E°_{Cat}$, which is analogous to the Bronsted catalysis law for general acid catalysis. This correlation, in conjunction with the Nernstian dependence of k_1/k_{-1} on $(E°_{Cat} - E°_M)$ and the earlier observed proportionality between k_2 values and uncatalyzed specific rates, leads to the equation $\log (k_1k_2/k_{-1}) = (E°_{Cat} - E°_M)F/2.3RT + 3.81 - 5.17E°_{Cat} + \log [k_{Ox}/k_{Co(py)}]_{un}$, which allows estimates of the specific rates of catalyzed electron-transfer reactions in which oxidant, reductant, and catalyst are independently varied. The final term in this equation is the ratio of specific rates, using a common reductant, for the uncatalyzed reduction of the oxidant chosen and for $Co(NH_3)_5py^{3+}$, the latter taken as a standard. This equation, when applied to 17 systems for which specific rates span six decades, yields values of $\log (k_1k_2/k_{-1})$ in agreement with the observed values to better than 0.38 log unit. Agreement is poorest for reactions catalyzed by the acidic form of isonicotinamide, for which k_2 and $E°$ are at present relatively uncertain.

Diverse heterocyclic species have been shown[2] to catalyze the reductions, using Eu^{2+} and V^{2+}, of such outer-sphere oxidants as $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, and $(en)_3Co^{3+}$. For such catalyzed reactions evidence has been presented[2] in support of the sequence

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

where "Cat·" is a substituted radical resulting from one-electron reduction of the catalyst. When the radical intermediate is present at small steady-state concentrations, the effectiveness of a given catalyst is generally proportional to the quotient k_1k_2/k_{-1}.[2a] Although the ratio k_1/k_{-1} is related, by the Nernst equation, to the formal potentials $E°_{M^{3+}-M^{2+}}$ and $E°_{Cat-Cat\cdot}$, no systematization of the various k_2 values has been reported.[3] In the present extension, we have examined the action of several additional catalysts having a relatively wide range of $E°$ values and have noted a linear dependence of $\log k_2$ on $E°_{Cat-Cat\cdot}$ which leads in turn to a simple relationship between potentials and catalytic potencies.

Experimental Section

Materials. Solutions of europium(II),[4,5] vanadium(II),[6] and chromium(II)[7] were prepared by published procedures. Cobalt(III) complexes were available from a previous study.[2a] Diquat (IV) was prepared by the procedure of Homer and Tomlinson;[8] other catalysts (Aldrich products) were used as received.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[2] All catalyzed reactions were first order each in reductant and catalyst. With nicotinamide, *N*-methylnicotinamide, and 3-benzoylpyridine as catalysts, only a single reductant, Eu^{2+}, and only one oxidant, $Co(NH_3)_5py^{3+}$, were used. With Eu^{2+} in excess, these reactions were first order in Co(III) and were inhibited by added Eu^{3+}. Rate measurements with these catalysts were generally made under pseudo-first-order conditions with either Co(III) or Eu^{2+} in greater than fivefold excess.

Diquat-catalyzed reactions were carried out with Eu^{2+}, V^{2+}, and Cr^{2+} as reductants and with $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$ as oxidants. Reductions by Cr^{2+} and Eu^{2+} were run with the ratio $[Red]/[Co^{III}]$ greater than 10, but for some reductions by V^{2+}, the oxidant was held in excess. Reductions by Cr^{2+} followed pseudo-zero-order kinetics with rates independent of $[Co^{III}]$; such reactions were unaffected by added Cr^{3+}. Reductions using excess V^{2+} were, however, first order in Co(III) and were inhibited by V^{3+}; with excess oxidant, rates were independent of Co(III). The kinetic character of the Eu^{2+}–diquat systems was analogous to that of the Cr^{2+} reductions, except for the Eu^{2+}–$Co(en)_3^{3+}$ reaction in the presence of >0.1 M Eu^{3+}, under which conditions it displayed pseudo-first-order kinetic curves and was inhibited by Eu^{3+}.

Measurements were made both in 1.0 M $HClO_4$ and near pH 5 (0.10 M HOAc + 0.10 M NaOAc + 0.90 M $LiClO_4$). Pseudo-first-order reactions were followed to at least 5 half-lives, and rate constants were obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Pseudo-first-order rate constants derived from replicate runs checked to within 8% and pseudo-zero-order constants to within 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Potentiometric Experiments. The reduction potential of diquat (IV) was estimated in 1.0 M $HClO_4$ by measuring the degree of conversion to the reduced form in various known mixtures of Eu^{2+} and Eu^{3+}. Measurements were carried out at 760 nm, at which wavelength the reduced (radical) form has an extinction coefficient of 3109[9] and the oxidized form a negligible absorptivity. The average of three such measurements, in conjunction with the standard potential −0.379 V reported for the Eu^{2+}/Eu^{3+} couple in a similar medium,[10] yielded $E° = -0.443 \pm 0.004$ V.

Results and Discussion

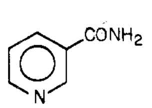
As in earlier studies,[2] kinetic data are interpreted in terms of rate law 2, obtained by application of the steady-state

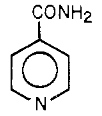
$$\text{rate} = \frac{k_1k_2[Co^{III}][M^{2+}][Cat]}{k_{-1}[M^{3+}] + k_2[Co^{III}]} + k_{un}[Co^{III}][M^{2+}] \tag{2}$$

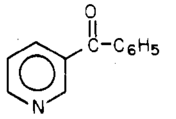
approximation to the intermediate, "Cat·", in sequence 1. The k_{un} term pertains to the uncatalyzed reaction. The competition between M^{3+} and Co(III) for Cat· determines the apparent kinetic behavior of these systems. When the k_{-1} term, representing reversal of the initial step, is dominant, the catalyzed reaction is first order in Co(III) and inhibited by M^{3+}. When the k_2 term in the denominator, arising from the reaction of Co(III) and Cat·, is large, the catalyzed rate becomes nearly independent of $[Co^{III}]$ and approaches $k_1[M^{2+}][Cat]$, the rate of the initial step.

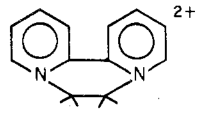
Representative kinetic data for the Eu^{2+} reduction of $Co(NH_3)_5py^{3+}$, as catalyzed by nicotinamide, I, appear in Table I. Since this amide is a much less effective catalyst than the γ-substituted pyridine derivatives described in earlier

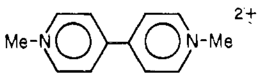
0020-1669/78/1317-1827$01.00/0


"NA", I


"INA", II


III


"DQ", IV


"MV", V

reports,[2a,b] catalyst concentrations are near 0.1 M, rather than 10^{-4} M. With Co(III) in deficiency and $[Eu^{2+}]$ held constant, plots of pseudo-first-order rate constants vs. $[Cat][Eu^{2+}]/[Eu^{3+}]$ are closely linear with slope k_1k_2/k_{-1} and intercept $k_{un}[Eu^{2+}]$.[11,12] With Co(III) in excess, plots of rate constants vs. [Cat] yield k_1 as slope. The resulting kinetic parameters for nicotinamide, and those obtained in an analogous manner for its *N*-methyl derivative and for 3-benzoylpyridine, III, are assembled in Table III.

Experiments with the catalyst diquat (IV), carried out with the reductants V^{2+} and Cr^{2+}, as well as with Eu^{2+}, are summarized in Table II. A number of reductions with this catalyst exhibited pseudo-zero-order kinetics with the reductant in excess, indicating $k_{-1}[M^{3+}]$ to be much smaller than $k_2[Co^{III}]$. For such reactions, plots of observed rates vs. the product $[M^{2+}][Cat]$ are linear with slope k_1. These specific rates are also included in Table II, as are values of k_2/k_{-1} obtained from the M^{3+}-inhibited reactions in the usual manner. Only k_1 can be obtained experimentally for Cr^{2+} reductions, since $k_{-1}[Cr^{3+}]$ is negligible in all cases. With Eu^{2+} as reductant, $k_{-1}[Eu^{3+}]$ can be made to exceed $k_2[Co^{III}]$ when the oxidant is $Co(en)_3{}^{3+}$ but not when it is the more reactive $Co(NH_3)_5py^{3+}$; hence k_2/k_{-1} values are entered only for the tris chelate.

Values of the quotient k_1k_2/k_{-1} for the amide catalysts may be divided by k_2's, obtained directly in pulse radiolytic experiments with the amides and cobalt(III) complexes in the absence of metal reductants,[13] to obtain k_1/k_{-1}. The latter ratio is, in our systems, related to the formal potential of the catalyst, $E°_{Cat}$, in accordance with the Nernst dependence; i.e.

$$\log (k_1/k_{-1}) = (E°_{Cat} - E°_{Red})F/2.3RT \qquad (3)$$

where $E°_{Red}$ is the potential of the reducing center. Values of k_1/k_{-1} for the amides, in combination with the standard potential −0.379 V for Eu^{2+}/Eu^{3+},[10] lead to the formal potentials in Table IV. Conversely, with methylviologen and diquat, for which $E°_{Cat}$ may be determined directly,[2c] the composite rate constant k_1k_2/k_{-1} may be used to calculate values of k_2.

The addition of nicotinamide and diquat to the array of catalytic species studied more than doubles the range of formal reduction potentials associated with the catalysts for which kinetic parameters have been determined. It is now apparent that k_2, as well as k_1/k_{-1}, depends on $E°_{Cat}$. Table IV lists k_2 values for the reactions of the catalyst radicals with $Co(NH_3)_5py^{3+}$, chosen as a reference oxidant. As expected, the most strongly reducing radicals react most readily. A plot of $\log k_2$ vs. $E°_{Cat}$ (Figure 1) approaches linearity with the regression line corresponding to the relationship

$$\log k_2 = 3.81 - 5.17E°_{Cat} \qquad (4)$$

Combination of (3) and (4) allows an estimate of the composite rates k_1k_2/k_{-1} of reduction of $Co(NH_3)_5py^{3+}$, using the various combinations of catalysts and single-electron reducing agents for which potentials are known, but another term must be added to extend the treatment to other oxidants.

Table I. Kinetic Data for the Europium(II) Reduction of Pyridinepentaamminecobalt(III), $(NH_3)_5pyCo^{3+}$, as Catalyzed by Nicotinamide

$10^3 \times [Co^{III}]$, M	$10^2 \times [Eu^{2+}]$, M	[Cat], M	$10^2 \times [Eu^{3+}]$, M	$[H^+]$, M	10^3k[a]
19.5	0.20	0.200	0	2×10^{-5} [b]	19
19.5	0.20	0.400	0		35
19.5	0.20	0.600	0		48
19.5	0.20	0.800	0		66
9.75	0.20	0.400	0		30
1.89	2.00	0.106	3.00		6.7
1.89	2.00	0.177	3.00		8.7
1.89	2.00	0.353	3.00		12
1.89	2.00	0.502	3.00		17
1.89	2.00	0.106	6.00		4.8
18.0	0.20	0.333	0	1.0[c]	3.9
18.0	0.20	0.500	0		5.3
18.0	0.20	0.583	0		6.2
9.0	0.15	0.583	0		4.7
1.8	2.00	0.223	2.00		1.2
1.8	2.00	0.500	2.00		1.8
1.8	3.47	0.500	2.00		2.9
1.8	2.00	0.500	1.00		3.2

[a] Pseudo-first-order specific rates, in s^{-1}, at 25 °C. [b] Reaction medium was 0.1 M NaOAc + 0.1 M HOAc + 0.9 M $LiClO_4$. The reported pK_A of HOAc in 1 M perchlorate is 4.61 (L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 364 (1964)). [c] Reaction medium was 1.0 M $HClO_4$.

Table II. Kinetic Data for Reductions of $Co(en)_3$ As Catalyzed by Diquat[a]

Reductant, M^{2+}	$10^3 \times [Co^{III}]$, M	$10^2 \times [M^{2+}]$, M	$10^3 \times$ [Cat], M	$10^2 \times [M^{3+}]$, M	k[b]
	Pseudo-Zero-Order Reductions				
Cr^{2+}	0.79	2.36	2.20	0	18
	1.57	2.36	2.20		18
	1.57	2.36	0.55		4.6
	1.57	1.18	1.10		5.2
Eu^{2+}	1.57	2.00	0.110	0	12.0
	1.57	2.00	0.22		22
	1.57	2.00	0.055		6.0
	1.57	2.00	0.165		17
	1.57	1.00	0.110		5.5
	1.57	3.00	0.110		17
	1.57	2.00	0.110	2.0	11
	1.90[c]	2.00	0.165	0	18
	1.90[c]	2.00	0.330		31
	1.90[c]	2.00	0.66		66
	1.90[c]	2.00	0.330		16
	Pseudo-First-Order Reductions				
Eu^{2+}	1.18	2.00	0.44	20.0	6.3
	1.18	2.00	0.22	10.0	6.3
	1.18	2.00	0.22	15.0	3.6
	1.18	2.00	0.22	20.0	2.9
	1.18	2.00	0.22	30.0	1.9
V^{2+}	24.4	0.14	1.10	0	2.0
	24.4	0.14	2.20	0	4.1
	24.4	0.14	3.30	0	6.9
	12.2	0.14	2.20	0	4.6
	1.18	2.81	2.20	0.70	4.3
	1.18	2.81	2.20	1.41	2.2

[a] Reactions at 25 °C. The supporting electrolyte was 1.0 M $HClO_4$, except for the first-order reductions by Eu^{2+} (0.1 M $HClO_4$ + enough $LiClO_4$ to bring μ to 1.0 M). [b] Pseudo-zero-order rate constants are in $M\ s^{-1} \times 10^6$. Pseudo-first-order rate constants are in $s^{-1} \times 10^3$. [c] The oxidant was $(NH_3)_5pyCo^{3+}$.

The Marcus model for outer-sphere electron-transfer reactions[14] predicts that relative rates for two oxidants with a common reductant are independent of the identity of the reductant. The reduced (radical) forms of catalysts of the type

Table III. Catalyzed Electron-Transfer Reactions: Kinetic Parameters[a]

Catalyst	Reductant	Oxidant	k_1	k_2/k_{-1}
Nicotinamide (pH 4.7)	Eu^{2+}	$Co(NH_3)_5py^{3+}$	0.10	0.36
Nicotinamide (1 M $HClO_4$) (HNA)	Eu^{2+}	$Co(NH_3)_5py^{3+}$	0.0073	4.10
N-Methylnicotinamide (pH 4.7)	Eu^{2+}	$Co(NH_3)_5py^{3+}$	0.5	0.019
3-Benzoylpyridine (III) (pH 4.7)	Eu^{2+}	$Co(NH_3)_5py^{3+}$	2.8[b]	14[b]
Diquat (IV)	Eu^{2+}	$Co(en)_3{}^{3+}$	5.3	2.7×10^2
	Eu^{2+}	$Co(NH_3)_5py^{3+}$	5.0	
	V^{2+}	$Co(en)_3{}^{3+}$	19	0.26
	Cr^{2+}	$Co(en)_3{}^{3+}$	0.38	

[a] Values of k_1 (see mechanism 1) are in $M^{-1}\ s^{-1}$. The ratio k_2/k_1 is dimensionless. Reaction temperatures were 25 °C. Reactions were generally carried out at unit ionic strength (see Tables I and II). [b] Kinetic parameters for this catalyst in 1.0 M $HClO_4$ are listed in ref 2b.

Table IV. Reductions of Pyridinepentaamminecobalt(III), $py(NH_3)_5Co^{3+}$, by Radicals Derived from Heterocyclic Catalysts

Catalyst	$E°$, V[a]	k_2,[b] $M^{-1}\ s^{-1}$	log k_2	log k_2[c]
Nicotinamide (NA) (pH 4.7)	−1.013	2.0×10^9	9.30	9.04
Nicotinamide, acidic form (HNA) (1 M $HClO_4$)	−0.956	2.5×10^8	8.40	8.75
Isonicotinamide (INA) (pH 4.7)	−0.764	1.8×10^8	8.26	7.76
Isonicotinamide, acidic form (HINA) (1 M $HClO_4$)	−0.660	2.7×10^6 [d]	6.43	7.12
Methylviologen (MV)	−0.515	4.5×10^6 [e]	6.65	6.47
Diquat (DQ)	−0.445	1.5×10^6 [e]	6.18	6.11

[a] Potentials of the amides obtained from a combination of kinetic and pulse radiolytic data (see text). Potentials for MV and DQ were obtained by spectrophotometric estimates of the concentration of reduced (radical) form in solutions having known Eu^{2+}/Eu^{3+} ratios (see Experimental Section and ref 2c). [b] Specific rates (25 °C, $\mu = 1.0$) for the reaction of the reduced (radical) form of the catalyst with $py(NH_3)_5Co^{3+}$ (eq 1) were obtained by combinations of kinetic, pulse radiolytic, and potentiometric data (see text). [c] Calculated from the relationship $\log k_2 = 3.81 - 5.17E°_{Cat}$ (see text). [d] Specific rate, k_2, for the reaction with $py(NH_3)_5Co^{3+}$ taken to be 0.9 times that for the reaction with the 4-$CONH_2$-substituted pyridine derivative (see ref 13). [e] Specific rate, k_2, for the reaction with $py(NH_3)_5Co^{3+}$ taken to be 88 times that for reaction with $Co(en)_3{}^{3+}$ (see ref 2a).

here considered have been shown to conform to this model within a wide range of activity;[2a] i.e., the ratio of k_2 values for a given pair of oxidants has been found to be very nearly the same for each catalyst and to correspond also to rate ratios for uncatalyzed reductions by the various metal centers. Hence, eq 5 may be used to estimate composite rates for

$$\log \frac{k_1 k_2}{k_{-1}} = (E°_{Cat} - E°_{Red})\frac{F}{2.3RT} + 3.81 - 5.17E°_{Cat} + \log \left[\frac{k_{ox}}{k_{Co(py)}}\right]_{un} \tag{5}$$

catalyzed reactions in which oxidant, reductant, and catalyst are independently varied. The final term in (5) is the ratio of specific rates, using a common reductant, for the uncatalyzed reductions of the oxidant at hand and for $(NH_3)_5Co(py)^{3+}$.[15]

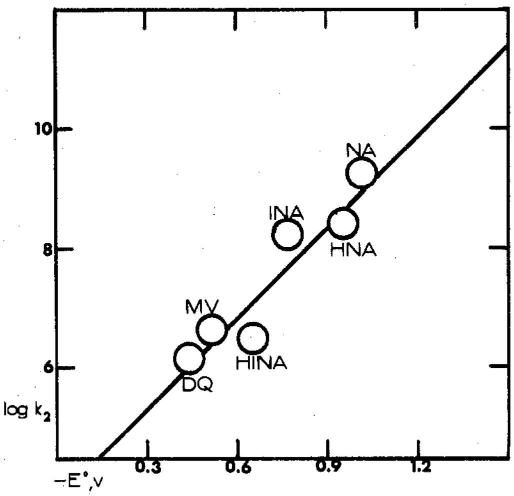


Figure 1. Comparison of the standard potentials for one-electron reduction of heterocyclic electron-transfer catalysis to values of log k_2, referring to the specific rates of reaction of the reduced (radical) forms of these catalysts with $py(NH_3)_5Co^{3+}$ (see eq 1) (25 °C, μ = 1.0). The least-squares line shown corresponds to the equation $\log k_2 = 3.81 - 5.17E°$.

Table V. Catalyzed Electron-Transfer Reactions: Composite Rate Constants

Reductant	Catalyst	Oxidant	log (k_1k_2/k_{-1}) Exptl[a]	log (k_1k_2/k_{-1}) Calcd[b]
U^{3+}	HNA	$Co(en)_3{}^{3+}$	1.36[c]	0.91
	HINA	$Co(en)_3{}^{3+}$	4.12[c]	4.19
Cr^{2+}	MV	$Co(en)_3{}^{3+}$	2.91[d]	2.69
	DQ	$Co(en)_3{}^{3+}$	3.69	3.51
Eu^{2+}	NA	$Co(NH_3)_5py^{3+}$	−1.44	−1.62
	HNA	$Co(NH_3)_5py^{3+}$	−1.52	−1.68
	INA	$Co(NH_3)_5py^{3+}$	1.75	1.28
		$Co(NH_3)_5(pyz)^{3+}$	0.97	0.89
		$Co(NH_3)_5(imid)^{3+}$	0.46	0.16
		$Co(en)_3{}^{3+}$	−0.32	−0.74
	HINA	$Co(NH_3)_5py^{3+}$	1.19[e]	2.50
		$Co(NH_3)_6{}^{3+}$	−0.06[e]	0.81
		$Co(NH_3)_5Me_3ac^{2+}$	0.10[e]	0.73[f]
	MV	$Co(en)_3{}^{3+}$	2.41[d]	2.17
	DQ	$Co(en)_3{}^{3+}$	3.16	3.00
V^{2+}	MV	$Co(en)_3{}^{3+}$	0.05[d]	−0.15
	DQ	$Co(en)_3{}^{3+}$	0.69	0.67
$Ru(NH_3)_6{}^{2+}$	DQ	$Co(NH_3)_5py^{3+}$	<-3.0	−5.0

[a] Specific rates (25 °C, $\mu = 1.0$) defined in eq 1). [b] Calculated using eq 5. [c] Unpublished experiments by M. K. Loar, Kent State University, 1977. [d] Reference 2c. [e] Reference 2a. [f] In this calculation, the estimated specific rate for the outer-sphere component of the catalyzed reaction[15] was used.

Calculated and experimental values of log (k_1k_2/k_{-1}), covering a range of six decades, are compared in Table V. The mean deviation between observed and calculated values is 0.38 logarithmic unit, with the quality of fit significantly lowered by the entries pertaining to reactions catalyzed by the acidic form of isonicotinamide (HINA), for which both k_2 and $E°$ are relatively uncertain.[16]

Apart from its approximate nature, the treatment is subject to important limitations. In order that the steady-state approximation apply, the intermediate Cat· must react rapidly enough so that its concentration remains far below those of the oxidant, reductant, and catalyst. Moreover, it must be in mobile equilibrium with $M^{3+}(aq)$. Hence, the treatment may not apply to Cr^{2+} sequences in which the initial act of electron transfer is inner sphere, resulting in a Cr(III)-bound radical.[17] Poor agreement is also expected for those very rapid oxidants which are found to be reduced by pyridine-derived radicals, with little or no selectivity,[2a,13] at rates 10^{-2}–10^{-1} times the diffusion-controlled limit. In addition, the value chosen for $(k_{Ox})_{un}$ must be an outer-sphere specific rate. For oxidants devoid of bridging groups, this may be observed directly. For others, an estimated partial specific rate associated with the outer-sphere component[15] may be used.

Equation 4, which links $\log k_2$ to $E°_{\text{Cat}}$, when rewritten as (6), is clearly related to the Bronsted catalysis law, (7), which

$$\log k_2 = 3.81 + 0.30\Delta G°_{\text{Cat}}/2.3RT \qquad (6)$$

$$\log k_{\text{HA}} = \text{constant} + B_{\text{A}}\Delta G°_{\text{HA}}/2.3RT \qquad (7)$$

correlates the specific rates, k_{HA}, of reactions subject to general acid catalysis with the acidities of the catalyzing acid.[18] The factor 0.30 in (6) is analogous to the Bronsted coefficient, B_{A}, in (7) and is generally considered to have parallel significance, i.e., a measure of the degree to which the electron (or proton) has been transferred from donor to acceptor in the activated complex.[14] Although there is no way in which the extent of transfer may be verified directly, we note that a proportionality constant well below $^1/_2$ in our system is that expected for a series of electron-transfer reactions in which values of $\Delta G°$ are very strongly negative.[19]

Finally, we point out that selectivity of the type thus far observed in electron-transfer catalysis is closely related to the positive but nonunit slope in (6). If, on one hand, this slope were zero (i.e., if the reactivities of the radical intermediates were independent of their structures), catalytic effectiveness would depend only on the steady-state concentration of such radicals and hence on the difference $E°_{\text{Cat}} - E°_{\text{Red}}$. At the other extreme, a unit slope in (6) would result in cancellation of the $E°_{\text{Cat}}$ terms in (5), catalytic activity would depend only on the oxidant and the reductant taken, and any kinetic advantage resulting from an increase in [Cat·] would be offset precisely by a decrease in k_2.

Acknowledgment. The authors are grateful to Mrs. Marilyn Loar for permission to cite her data prior to publication. We also thank Dr. L. Meites and Dr. E. Hayon for valuable discussions.

Registry No. $Co(NH_3)_5py^{3+}$, 31011-67-3; $Co(en)_3^{3+}$, 14878-41-2; $Co(NH_3)_5(pyz)^{3+}$, 59389-55-8; $Co(NH_3)_5(imid)^{3+}$, 38716-02-8; NA, 98-92-0; *N*-methylnicotinamide, 3106-60-3; 3-benzoylpyridine, 5424-19-1; HINA, 40617-90-1; MV, 4685-14-7; DQ, 2764-72-9; HNA, 38719-50-5; INA, 1453-82-3; V^{2+}, 15121-26-3; Cr^{2+}, 22541-79-3; U^{3+}, 22578-81-0; $Ru(NH_3)_6^{2+}$, 19052-44-9; Eu^{2+}, 16910-54-6.

References and Notes

(1) Sponsorship of this work by the National Science Foundation (Grant CHE74-03876 A01) is gratefully acknowledged.

(2) (a) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *J. Am. Chem. Soc.*, **99**, 1073 (1977); (b) Y.-T. Fanchiang, J. C. Thomas, V. D. Neff, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **16**, 1972 (1977); (c) Y.-T. Fanchiang and E. S. Gould, *ibid.*, **16**, 2516 (1977).

(3) Although we have pointed out[2b] that effective catalysts of this sort exhibit quasi-reversible reduction peaks (1 M $HClO_4$, 25 °C) in the range −0.53 to −0.81 V (vs. SCE), such a correlation is clearly approximate. Within this range there is no apparent relationship between observed potential and catalytic effectiveness.

(4) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).

(5) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).

(6) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(7) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(8) R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 2498 (1960).

(9) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972).

(10) G. Biedermann and H. R. Silber, *Acta Chem. Scand.*, **27**, 3761 (1973).

(11) The extrapolated k_{un} value, 0.21 $M^{-1}\ s^{-1}$, for the Eu^{2+} reduction of $Co(NH_3)_5py^{3+}$ in acetate buffer is about 2.5 times the reported[5] specific rate in 1 M $HClO_4$. The difference doubtless reflects catalysis of the reaction by the acetate anion, in close analogy to the anion catalyses described by Przystas and Sutin.[12] The latter catalyses are of much smaller magnitude than, and unrelated to, the electron-transfer catalyses here described. In an independent experiment (R. Reid, M. Sc. Thesis, Kent State University, 1976), the rate of V^{2+} reduction of $Co(NH_3)_5py^{3+}$ has been found to be doubled by addition of 0.05 M HSO_4^- (μ = 1.0, 25 °C).

(12) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).

(13) H. Cohen and D. Meyerstein, *Isr. J. Chem.*, **12**, 1049 (1974).

(14) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(15) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974). Note that the k values in the final term of (5) need not pertain to the same reducing center as does $E°_{\text{M}}$ in the initial term.

(16) Experiments with only a single pulse radiolytic system involving HINA and cobalt(III), leading to values of both k_2 and $E°$ for this catalyst, appear to have been reported.[13]

(17) See, for example, Y.-T. Fanchiang, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **17**, 1142 (1978).

(18) See, for example: (a) P. R. Wells, "Linear Free Energy Relationships", Academic Press, London, 1968, pp 89–92; (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, pp 235–242. Note that in eq 7 the strength of the catalyzing acid is given as $\Delta G°_{\text{HA}}$, the standard free energy of its ionization.

(19) (a) N. S. Hush, *Trans. Faraday Soc.*, **57**, 557 (1961); (b) see also M. Chou, C. Creutz, and N. V. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1977).