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Electron Transfer. 33. Rate Enhancement by External Pyridinedicarboxylato Derivatives[1]

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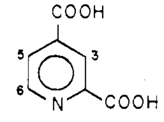
The reductions, using Eu^{2+} and Cr^{2+}, of such outer-sphere oxidants as $Co(NH_3)_5py^{3+}$ and $Co(en)_3^{3+}$ are strongly accelerated by derivatives of pyridinedicarboxylic acids. In the Cr^{2+} systems, the carboxylate species is consumed during the course of the reaction and thus does not function as a true catalyst. The Eu^{2+} reductions are straightforward and, as in earlier work,[4] are interpreted in terms of a sequence in which the catalyst is reduced (k_1) to a radical intermediate, after which this intermediate may participate in reversal of the initial step (k_{-1}) or may react with Co(III) (k_2). Differences in catalytic effectiveness exhibited by the various dicarboxylato derivatives reflect principally differences in k_1, which is greatest when both carboxyl groups are conjugated with ring nitrogen and least when neither group is conjugated. In the Cr^{2+} sequence, the active intermediate appears to be a Cr(III)-bound radical which, because of slow substitution at the Cr(III) center, is not in rapid equilibrium with $Cr(H_2O)_6^{3+}$. Kinetic data for Cr^{2+} reductions as accelerated by the methyl ester of 2,4-pyridinedicarboxylic acid (Est) allow calculation of: k_1, pertaining to formation of the radical-ion intermediate $Cr^{III}Est\cdot$; the ratio k_{-1}/k_2, which governs the competition between reversal of the initial step and reaction of $Cr^{III}Est\cdot$ with Co(III); K_A, the acidity constant of the catalytically inactive conjugate acid of the diester. The selectivity exhibited by $Cr^{III}Est\cdot$ toward the various Co(III) oxidants in this study corresponds closely to that displayed by unbound pyridyl radicals and also by reducing metal ion centers in uncatalyzed reactions. Evidence is presented that the reaction of Cr^{2+} with 2,4-pyridinedicarboxylic acid can yield two different radical ions, one of which is much more reactive toward Co(III) centers than is the other.

Of the various organic compounds which display external catalytic action in outer-sphere electron-transfer reactions between metal centers,[2] the most effective are related to 2,4-pyridinedicarboxylic acid (I). Catalysis of electron transfer by this diacid was first described in 1973,[3] and a later communication[4] presented kinetic data on Eu^{2+} and V^{2+} reductions as catalyzed by derivatives of this acid.



I

The present report describes extensions of our catalytic studies to include (1) catalysis of Eu^{2+} reductions by several isomeric pyridinedicarboxylic acids and (2) acceleration of Cr^{2+} reductions by derivatives of the 2,4-acid. The latter reactions are complicated by the possibility of coordination of Cr(III) to the catalytic center, leading to some curious mechanistic nuances.

Experimental Section

Materials. Lithium perchlorate[5] and solutions of Eu(II)[6] and Cr(II)[7] were prepared as described. Those cobalt(III) complexes not available from previous studies[2c,4] were prepared as described.[8] The 4-amide and the diester of 2,4-pyridinedicarboxylic acid were prepared by the method of Thunus,[9] the N-methylated 2,4-diacid by the procedure of Meyer,[7,10] and the N-methylated 2,4-diester by treatment of the diester with dimethyl sulfate for 5 h at 130 °C, in accordance with the procedure described by van Bergen and Kellogg.[11] Other catalysts were Aldrich products and were used as received.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[2c,6a,8a] Reactions were first order each in reductant and catalyst, and Eu(II) reactions carried out with the reductant in excess were first order in Co(III) as well. Catalyzed reactions of Eu^{2+} were inhibited by added Eu^{3+}, but Cr^{2+} reductions were not inhibited by Cr^{3+} in concentrations as great as 0.27 M. Reductions with Eu^{2+} were not significantly dependent on acidity in the range 0.1–1.2 M H^+. Most Eu^{2+} reductions were carried in 1.2 M $HClO_4$ with enough $LiClO_4$ added to bring the total ionic strength to 1.5 M, whereas Cr^{2+} reactions were generally run at $\mu = 1.0$. To evaluate effects of large variations in [Cr^{3+}], several runs were performed with added $Cr(ClO_4)_3$ + $Al(ClO_4)_3$, with the total concentration of tripositive ions 0.27 M. Pseudo-first-order reactions were followed to at least 4 half-lives, and rate constants obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Rate constants from replicate runs checked to within 7%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Table I. Spectra of Products Resulting from Reaction of Cr^{2+} with Derivatives of 2,4-Pyridinedicarboxylic Acid (I)[a]

Reagent	λ_{max}, nm	ϵ_1, M^{-1} cm^{-1}	λ_{max}, nm	ϵ_2, M^{-1} cm^{-1}
2,4-Diacid (I)	400	47	542	32
N-Methyl diacid	413	21	570	21
4-Amide	400	71	544	44
2,4-Dimethyl ester[b]	403	41	552	29
2,4-Dimethyl ester + Co(III)[c]	400	40	542	37

[a] 25 °C, 1.0 M $HClO_4$. Reactions were generally carried out with a slight excess of Cr^{2+}, and extinction coefficients calculated assuming complete reaction of the heterocyclic reagent. [b] Purple product from this reaction formed at a measurable rate (see text). [c] Chromium(III) product formed in the reaction of $Co(NH_3)_5py^{3+}$ with Cr^{2+} in the presence of the diester, then separated from the resulting reaction mixture by cation exchange. This species was eluted from polystyrenesulfonate resin using 4.5 M $NaClO_4$ (see ref 12).

Chromium(II) Reactions in the Presence of 2,4-Pyridinedicarboxyl Dervatives. Addition of Cr^{2+} to strongly acidic solutions of 2,4-pyridinedicarboxylic acid, its *N*-methyl derivative, or its 4-amide yielded, during the time of mixing, purple materials having similar, but not identical, visible spectra (Table I). The resulting solutions, in each case, reduced neither $(NH_3)_5CoCl^{2+}$ nor $(NH_3)_5pyCo^{3+}$. When, however, a deficiency of Cr^{2+} was added to a mixture containing a 5/1 mole ratio of $(NH_3)_5pyCo^{3+}$ to the dicarboxylato compound, Co^{III} was immediately reduced in quantity nearly equivalent, in all three cases, to Cr^{2+} added. Attempts to obtain satisfactory kinetic data for these catalyzed reactions by operating at very low catalyst levels were unsuccessful.

The reaction of the diacid with Cr^{2+} in 1.2 M $HClO_4$ was also examined under stop-flow conditions. A strongly absorbing species (λ_{max} near 410 nm, ϵ 6 × 10^2) was formed within the time of mixing (0.005 s) and decayed with a bimolecular rate constant of about 7 × 10^4 M^{-1} s^{-1}. The concentration of this pigment rose sixfold as the ratio diacid/Cr^{2+} was increased from 5/1 to 100/1, but reached a limiting value at very high concentrations of diacid. With [Cr^{2+}] at the 10^{-3} M level, half-conversion was observed with (diacid) near 0.02 M. This species did not react with $(NH_3)_5pyCo^{3+}$. Its formation and

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Table II. Representative Kinetic Data for the Reductions of Pyridinepentaamminecobalt(III), $(NH_3)_5pyCo^{3+}$, in the presence of 2,4-Pyridinedicarboxylic Acid Dimethyl Ester (Est)

Reductant M^{2+}	$10^3[Co^{III}]$, M	$10^2[M^{2+}]$, M	$10^4[Est]$, M	$10^2[M^{3+}]$, M	$[H^+]$, M	10^2k_{obsd}[a]	10^2k_{calcd}[b]
Eu^{2+}	3.26	2.00	0	0	1.2	0.17	
	2.00	2.00	0.044	4.00		5.0	4.3
	2.00	4.00	0.044	4.00		9.2	8.6
	2.00	2.00	0.088	4.00		8.7	8.6
	2.00	2.00	0.044	2.37		5.8	6.3
	2.00	2.00	0.044	5.33		3.3	3.3
	19.3	0.20	0.553	0		8.7	8.9
	19.3	0.20	0.277	0		4.3	4.3
	19.3	0.20	0.166	0		2.9	2.7
	9.7	0.20	0.277	0		4.3	4.3
Cr^{2+}	5.20	0.10	0	0	1.0	0.0021	
	5.20	0.10	46.9	0	1.0	6.2	6.1
	10.4	0.10	46.9	0	1.0	8.4	9.2
	20.8	0.10	46.9	0	1.0	12.5	12.3
	31.2	0.10	46.9	0	1.0	13.5	13.8
	41.6	0.10	46.9	0	1.0	16.0	14.8
	10.4	0.10	31.2	0	1.0	5.4	6.1
	10.4	0.10	46.9	0	1.0	8.4	9.2
	10.4	0.10	62.5	0	1.0	13.9	12.2
	10.4	0.10	93.8	0	1.0	23	19
	5.00	0.10	46.9	0	0.80	6.9	6.6
	5.00	0.10	46.9	0	0.60	8.9	7.5
	5.00	0.10	46.9	0	0.30	9.9	9.6
	5.00	0.10	46.9	0	0.20	12.6	12.0
	5.00	0.10	46.9	0	0.10	12.6	14.0
	1.92	2.00	34.7	0[c]	1.0	9.2[d]	
	1.92	2.00	34.7	10.0[e]	1.0	8.7[d]	
	1.92	2.00	34.7	27.0[f]	1.0	8.7[d]	

[a] Pseudo-first-order specific rates, in s^{-1}, at 25 °C. Except where indicated, μ was 1.5 M for Eu^{2+} reductions and 1.0 M for Cr^{2+} reductions ($LiClO_4$–$LiClO_4$). [b] Specific rates for Eu^{2+} reductions were calculated using eq 2 in text; those for Cr^{2+} reductions were calculated using eq 6. [c] Supporting electrolyte was 0.27 M $Al(ClO_4)_3$ + 1.0 M $HClO_4$. [d] Specific rate observed during the early stages of reaction. [e] Supporting electrolyte was 0.17 M $Al(ClO_4)_3$ + 0.10 M $Cr(ClO_4)_3$ + 10.0 M $HClO_4$. [f] Supporting electrolyte was 0.27 M $Cr(ClO_4)_3$ + 1.0 M $HClO_4$.

decay were not observable in 0.24 M $HClO_4$.

The reaction of Cr^{2+} with the dimethyl ester of I yielded no immediate color, but a purple pigment, similar to that from the parent acid, was slowly formed. Development of this color was first order in both reagents with an apparent rate constant about 0.2 $M^{-1}\ s^{-1}$ at 25 °C. Such a pigment could not be generated from the N-methylated diester. The "unblocked" diester accelerated the reductions of such slowly reacting Co(III) complexes as $Co(en)_3^{3+}$ and the $(NH_3)_5Co^{III}$ derivatives of pyridine, pyrazole, and imidazole, but in these cases, *1 mol of active ester was consumed by each mole of* Cr^{2+} *reacting*. Reproducible kinetic data for these ester-promoted reactions were obtained only if they were carried out so that at no time were Cr^{2+} and the diester present together in the absence of Co(III).

Cation-exchange separations of Cr(III) preparations were carried out using the Bio-Rad resin AG 50W-X2, 200–400 mesh, as described.[12]

Results and Discussion

Europium(II) Reductions. Catalyzed reductions by Eu^{2+} have been shown[2bc] to proceed through the sequence

$$\text{cat} \xrightleftharpoons[\mathrm{Eu}^{3+},\ k_{-1}]{\mathrm{Eu}^{2+},\ k_1} \text{cat}\cdot \xrightarrow[k_2]{\mathrm{Co^{III}}} \text{cat} + \mathrm{Co}^{2+} \tag{1}$$

where "cat·" is a substituted pyridyl radical, present at small steady-state concentrations.[2c,4] If the steady-state approximation is applied to this intermediate, this mechanism yields, for the rate of the catalyzed reaction

$$\text{rate} = \frac{k_1k_2[\mathrm{Co^{III}}][\mathrm{Eu^{2+}}][\text{cat}]}{k_{-1}[\mathrm{Eu^{3+}}] + k_2[\mathrm{Co^{III}}]} \tag{2}$$

When Eu^{2+} is in large excess, catalyzed reactions are first order in Eu^{2+}, Co^{III}, and catalyst and are inhibited by added Eu^{3+}, in accord with this expression. When, on the other hand, Co^{III} is in large excess, reactions are very nearly zero order in oxidant, for under such conditions, $k_1[Eu^{2+}][cat]$, representing the initial step, becomes rate determining.

Table III. Kinetic Parameters for Europium(II) Reductions of Pyridinepentaamminecobalt(III), $py(NH_3)_5Co^{3+}$, as Catalyzed by Pyridinedicarboxylato Derivatives

Catalyst substituents	k_1[a]	k_2/k_{-1}
N-CH_3-2,4-$(COOCH_3)_2$	5.2×10^3	2.8
2,4-$(COOCH_3)_2$	1.6×10^3	13
2,4-$(COOH)_2$[b]	1.7×10^3	7.5
N-CH_3-2,4-$(COOH)_2$[b]	1.5×10^3	22
2,5-$(COOH)_2$	8.4×10^2	6.2
2,5-$(COOCH_3)_2$	6.3×10^2	14
2,6-$(COOH)_2$[b]	1.8×10^2	1.1
3,4-$(COOH)_2$	1.6×10^2	4.3
2,3-$(COOH)_2$	26	4.9
4-COOH[c]	14	5.2
3,5-$(COOH)_2$	4.3	4.5

[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 conditions are listed in Table II. [b] See ref 4. [c] See ref 2c.

Representative data for a typical catalyzed system, the Eu^{2+} reduction of the pyridine complex, as catalyzed by the dimethyl ester of 2,4-pyridinedicarboxylic acid, are given in Table II. With Co^{III} in deficiency, plots of the pseudo-first-order rate constant vs. $[cat][Eu^{2+}]/[Eu^{3+}]$ are linear with slope k_1k_2/k_{-1}. With Co^{III} in excess, plots of rate constants vs. [cat] yield k_1 (as slope). The resulting parameters for the present series of catalysts are summarized in Table III. Individual values of k_{-1} and k_2 cannot be obtained from steady-state experiments alone.

Catalytic effectiveness, under the usual conditions, may be taken as proportional to k_1k_2/k_{-1}. The considerable range in catalytic power within this series is seen to result principally from variations in k_1, rather than in k_{-1}/k_2. Evidence has been presented[4] that the reaction of Eu^{2+} with catalysts of this type is an inner-sphere process, and since no appreciable loss in catalytic activity results from methylation of the carboxyl or

Table IV. Chromium(II) Reductions of Cobalt(III) Complexes in the Presence of 2,4-Pyridinedicarboxylic Acid Dimethyl Ester: Kinetic Parameters[a]

Oxidant	k_1[b]	k_2/k_{-1}[b]
$Co(NH_3)_5(pyridine)^{3+}$	94	92
$Co(NH_3)_5(pyrazole)^{3+}$	85	31
$Co(en)_3{}^{3+}$		1.3[c]

[a] Reactions carried out at 25 °C; $\mu = 1.0$. [b] Both k_1 and the ratio k_2/k_{-1} (see sequence 3) are in $M^{-1}\ s^{-1}$. Plots of $[Est]/k_{obsd}$ vs. $1/[Co^{III}]$ yield $1/k_1$ as intercept and k_{-1}/k_1k_2 as slope. [c] The small value of k_2 for this oxidant prevents experimental determination of k_1 by our procedures. The latter was assumed to be 94 $M^{-1}\ s^{-1}$, i.e., the value determined for the pyridine oxidant.

from methylation of the ring, attack of Eu^{2+} may be presumed to occur at a carbonyl group of the catalyst. Beyond that, the precise structural features governing catalytic activity remain elusive, although it may be noted that in the most powerful catalysts both carboxyl groups lie in conjugation with the heteronitrogen, whereas in the least effective 3,5-catalyst, neither carboxyl is so conjugated.

Chromium(II) Reductions. Reproducible kinetic data for reductions by Cr^{2+} in the present series were obtained only for those reactions accelerated by the 2,4-diester. Since the latter is found to be consumed, it cannot be said to function as a true catalyst in the manner observed for the corresponding Eu^{2+} system. Note also that chromium(II) reductions are retarded by addition of acid but not by Cr^{3+}.

Consumption of the diester and the observed insensitivity of reaction rate toward added Cr^{3+} require that catalytic sequence 1 be modified

$$\text{Est} \underset{k_{-1}}{\overset{Cr^{2+},\ k_1}{\rightleftharpoons}} Cr^{III}\text{Est}\cdot \xrightarrow[k_2]{Co^{III}} Cr^{III}\text{Est} + Co^{2+} \tag{3}$$

Here, the active intermediate derived from the accelerating pyridine diester is represented as $Cr^{III}Est\cdot$, a chromium(III)-bound ester radical cation, analogous to radical cations reported in Cr^{2+} pyrazine systems.[13] Because substitutions at Cr(III) centers are slow, $Cr(H_2O)_6{}^{3+}$ cannot reoxidize this intermediate and, hence, is without effect on the reaction rate.

Representative kinetic data for Cr^{2+} reductions appear in Table II. As is the case with systems featuring true catalysis, rates are proportional to the concentration of the added heterocycle. The $[H^+]$ dependence for this reaction fits the relationship

$$k_{obsd} = \frac{k_{lim}}{[H^+]/K_A + 1} \tag{4}$$

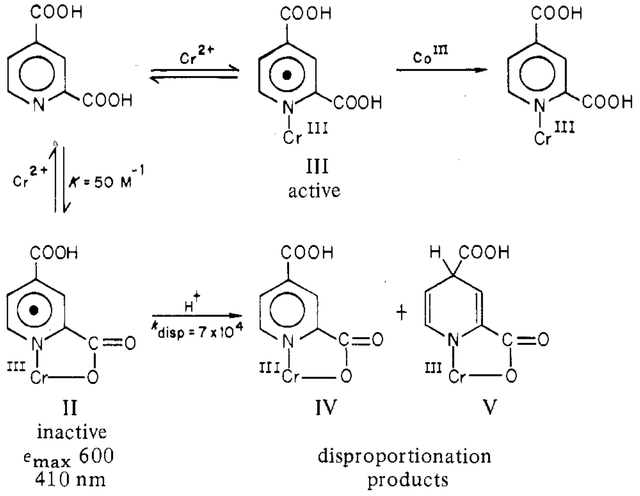
where k_{lim} is the specific rate at very low acidity. Equation 4 indicates partition of one of the reagents into an inactive protonated form, having an acidity constant K_A, and an active deprotonated form. Since neither $Cr(H_2O)_6{}^{2+}$ nor $Co(NH_3)_5py^{3+}$ has a pK_A near the pH range examined, the protonation equilibrium must involve the diester. A plot of $1/k_{obsd}$ vs. $[H^+]$, with the concentrations of the other reagents held constant, allows us to estimate[14] a K_A value of 0.80 for the diester, an acidity constant reasonable for a compound of this type.[15]

Application of the steady-state approximation to $Cr^{III}Est\cdot$ in sequence 3, in combination with the observed acidity pattern, gives the rate law

$$\text{rate} = \frac{k_1k_2[Co^{III}][Cr^{2+}][Est]}{(k_{-1} + k_2[Co^{III}])([H^+] + K_A)} \tag{5}$$

pertaining to the Cr^{2+}–diester systems. This expression is in accord with our kinetic data. Values of k_1 and the ratio k_2/k_{-1} giving the best agreement between calculated and observed rates are listed in Table IV. Pseudo-first-order specific rates calculated from these parameters are compared to observed rates in Table III. Similar kinetic treatment of the reductions of $Co(NH_3)_5(pyrazole)^{3+}$ and $Co(en)_3{}^{3+}$ lead to analogous parameters for these oxidants as well. Agreement between values of k_1 (which should be independent of the oxidant taken) for the cobalt(III)–pyridine and cobalt(III)–pyrazole systems is seen to be satisfactory.[16] Although individual values of k_2 cannot be calculated from the data at hand, they lie in the ratio 70:23:1, thus conforming quite closely to the corresponding ratio (80:37:1) for reaction of the noncoordinated 4-pyridinecarboxylato radical with the same oxidants.[2c] Hence, the selectivity exhibited by the Cr(III)-bound radical intermediate toward the various Co(III) oxidants in this work appears to be nearly the same as that displayed by unbound pyridyl radicals, in accordance with the Marcus picture for outer-sphere electron-transfer processes.[17] Very similar patterns have been shown to apply also to uncatalyzed outer-sphere reductions by metal ion centers.[2c,18]

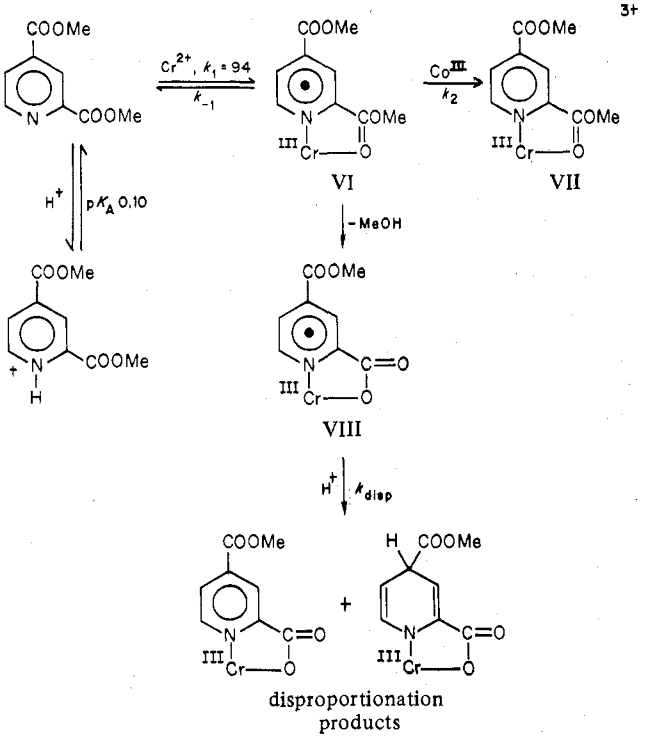
Scheme I



Our experiments further indicate that two different Cr(III) radical cations may be formed from the action of Cr^{2+} on the 2,4-diacid (Scheme I). The strongly absorbing species, λ_{max} 410 nm (ϵ >600), having a formation constant approximately 50 M^{-1} and a specific rate of bimolecular decay about 7×10^4 $M^{-1}\ s^{-1}$, is here represented as the chelated cation radical, II. Since this species is found not to react with $(NH_3)_5Co(py)^{3+}$, it cannot be the active intermediate in the accelerated redox sequence. For the latter, we suggest the nonchelated radical cation III. It appears that in the absence of a rapid external oxidant (such as tripositive cobalt), radical III is converted to II, which is the more stable of the two.[19] The spectrum of the chromium(III) product ultimately formed from Cr^{2+} and the diacid in the absence of cobalt(III) suggests a 1:1 mixture of chelated[20] disproportionation products, IV and V. The latter two species would be expected to exhibit very similar visible spectra.

The spectrum and elution behavior[21] of the Cr(III) product from the reaction of Cr^{2+} and $Co(NH_3)_5py^{3+}$ in the presence of the 2,4-diester (Scheme II) are consistent with the tripositive chelate VII, thus implying radical cation VI as the active intermediate in the diester sequence. With Co(III) absent, this intermediate is converted instead to blue Cr(III) product(s) very similar to that arising from the diacid (Table I). The development of the blue color in this instance, however, is slow and is found to be first order both in Cr^{2+} and diester, indicating the intervention of a slow step between formation of radical ion VI and its disproportionation. It is suggested that hydrolysis of the 2-COOMe group is occurring, yielding the chelated radical VIII, which is closely analogous to II and

Scheme II



which should undergo rapid disproportionation in the same manner.[22-24]

Registry No. $Co(NH_3)_5py^{3+}$, 31011-67-3; $Co(NH_3)_5(pyrazole)^{3+}$, 38671-07-7; $Co(en)_3{}^{3+}$, 14878-41-2; N-CH_3-2,4-$(COOCH_3)_2(NC_5H_3)$, 65878-79-7; 2,4-$(COOCH_3)_2(NC_5H_3)$, 25658-36-0; 2,4-$(COOH)_2(NC_5H_3)$, 499-80-9; N-CH_3-2,4-$(COOH)_2(NC_5H_3)$, 62778-02-3; 2,5-$(COOH)_2(NC_5H_3)$, 100-26-5; 2,5-$(COOCH_3)_2(NC_5H_3)$, 881-86-7; 2,6-$(COOH)_2(NC_5H_3)$, 499-83-2; 3,4-$(COOH)_2(NC_5H_3)$, 490-11-9; 2,3-$(COOH)_2(NC_5H_3)$, 89-00-9; 4-$COOOH(NC_5H_4)$, 55-22-1; 3,5-$(COOH)_2(NC_5H_3)$, 499-81-0; 2-COOH-4-$CONH_2(NC_5H_3)$, 24195-08-2; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6.

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(14) The intercept of such a plot is $1/k_{lim}$, whereas the slope is $1/K_Ak_{lim}$.

(15) R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956), report that incorporation of a 2-COOMe group on the pyridine ring decreases pK_A of the parent heterocycle (pK_A 5.17) by 3 units, whereas incorporation of 4-COOMe decreases pK_A by 2 units. The pK_A 0.10, obtained here for the 2,4-diester, suggests that these substituent effects are additive.

(16) Note that as a consequence of the low k_2 value for $Co(en)_3{}^{3+}$, reductions of this complex, as accelerated by the diester, are first order in Co(III), whereas with the pyridine- and pyrazole-bound oxidants (see, for example, Table II), Co(III) dependency is less steep than that corresponding to a first-order relationship.

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

(18) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974).

(19) This change almost certainly does not occur by substitution at the Cr(III) center, which is slow, but rather through redissociation of II to Cr^{2+} and the parent 2,4-diacid. The implication here is that the steady state involving the more stable radical II is more slowly established than that involving radical cation III.

(20) See, for example, E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(21) See, for example, E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).

(22) The proposed sequence for the formation of the blue product(s) from the diester in the absence of Co(III)

$$Cr^{2+} + Est \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} VI\cdot \xrightarrow{k_2} VIII\cdot$$

$$2VIII\cdot \xrightarrow{k_3} \text{products}$$

leads, assuming the steady-state approximation to be applicable to VI· and VIII·, to the rate law

$$\text{rate} = \frac{k_1k_2[Cr^{2+}][Est]}{k_2 + k_{-1}}$$

(23) Powerful catalysis of the hydrolysis of ester groups by coordinated metal ions has long been known.[24] Why such hydrolysis should occur in radical ion VI, but not in chelate VII, remains a puzzling point.

(24) See, for example: (a) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957).

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Electrochemistry of Iron Phthalocyanine Complexes in Nonaqueous Solvents and the Identification of Five-Coordinate Iron(I) Phthalocyanine Derivatives

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An electrochemical study (cyclic voltammetry, dc polarography, and differential-pulse polarography) of iron(II) phthalocyanine was carried out in pyridine, dimethyl sulfoxide, and dimethylacetamide with various supporting electrolytes. Oxidation to iron(III) and reduction to an iron(I) complex and an iron(I) phthalocyanine radical anion species were observed. Analysis of the cyclic voltammetry provided evidence for several following chemical reactions. The iron(I) complexes were shown to be five-coordinate and were characterized by electron spin resonance. A considerable dependence of the various redox couples upon the nature of the solvent and upon the supporting electrolyte was noted and explained. In this fashion back-donation was shown to be an important factor in the stabilization of the iron(II) species. The iron(I) phthalocyanines are low-spin d^7 complexes with a $d_{z^2}{}^1$ ground state. Superhyperfine coupling to axially coordinated pyridine, imidazole, and triphenylphosphine was observed.

It is now well established[1] that redox processes of iron-containing moieties play an indispensable role in biological electron-transfer processes. Intimately involved with this role is the ability of molecules such as hemoglobin and myoglobin

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