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Electron Transfer. 63. Catalysis by N-Substituted Isonicotinoyl Derivatives[1]

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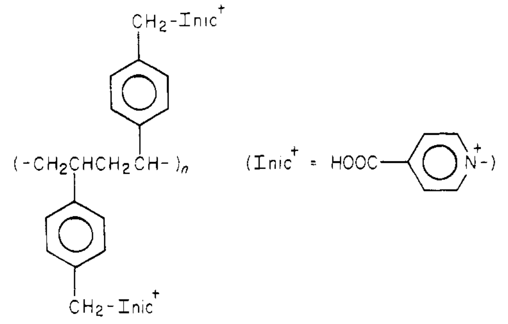
Isonicotinoyl derivatives featuring *N*-aryl- or *N*-benzyl-type substituents catalyze the outer-sphere reductions of Co(III) by Eu^{2+} much more effectively than does the prototype electron-transfer catalyst *N*-methylisonicotinic acid. Enhanced catalytic potency arises from an increased rate at which the catalyst is converted to the reactive radical intermediate (cat·), rather than a tilting of the competition between Eu^{3+} and Co(III) for this radical. Evidence is presented that the improvement reflects increased stabilization of the radical by inductive electron withdrawal from the pyridine ring rather than by conjugative delocalization of the unpaired electron. The *N*-phenyl- and *N*-naphthyl-substituted species are among the most effective catalysts of this type thus far reported. Moreover, deterioration of these new catalysts under conditions of use is found to be much less severe than that of the very active catalysts described earlier. The observation that the present catalysts are just as effective as the earlier *N*-carboxymethyl catalyst (XI) weighs against the proposed intervention of a homoallylic-type intermediate (XV) in the catalytic sequence. The 3-pyridyl-substituted cation (IX), which forms the most stable radical (XVII) in the present series, is catalytically inactive, in accord with the low reactivity observed for pyrazinium and quinoxalinium radicals, to which radical XVII is structurally analogous.

In earlier studies describing the catalysis of electron-transfer reactions between metal centers by uncoordinated pyridine derivatives, it was pointed out that the most effective catalysts of this type often suffer severe deterioration with use.[2] Such catalysts operate by preliminary reduction to a radical intermediate, cat·, which then reacts with the oxidant, and it has been shown[2b,c] that a major mode of catalytic attrition entails rapid disproportionation of the radical (eq 1). On this

$$2\text{cat}\cdot \xrightarrow{2\text{H}^+} \text{cat} + \text{catH}_2 \qquad (1)$$

basis, we hoped that incorporation of the catalytic center into a polymeric chain of type I, thus decreasing its mobility, would minimize this side reaction, resulting in improved recycling properties for the catalyst. Since the proposed polymeric catalyst I is, in effect, an *N*-benzylisonicotinic acid derivative, it seemed reasonable, for comparison, to examine briefly the catalytic properties of its monomeric analogue, *N*-benzylisonicotinic acid. Somewhat unexpectedly, this monomer proved to be significantly more effective than the corresponding *N*-methyl acid, one of the prototype outer-sphere catalysts.[2a] Further substantial improvement resulted when the phenyl group was attached directly to the pyridine nitrogen. Indeed, the catalytic effectiveness of certain of these N-arylated isonicotinoyl derivatives proved to be comparable to that of the methyl ester of 2,4-pyridinedicarboxylic acid, the most powerful catalyst of the type thus far studied.[2c] Moreover, decay of our new catalysts under the usual reaction conditions is found to be much less marked than that of the similarly active catalysts previously described.



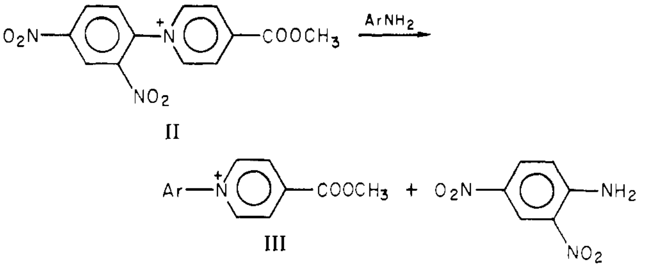
I

Experimental Section

Inorganic Materials. (Pyridine)pentaamminecobalt(III) perchlorate, $\text{Co(NH}_3)_5\text{py(ClO}_4)_3$,[3] the primary oxidant, and solutions of $\text{Eu(ClO}_4)_2$,[4] the primary reductant, were prepared as described.

Catalysts. *N*-Benzyl- and related *N*-arylmethyl-substituted catalysts were prepared by N-alkylation of sodium isonicotinate (in water) or methyl isonicotinate (in the absence of solvent) using the appropriate bromomethyl or chloromethyl aromatic as described.[5] Attempted N-alkylations using β-(bromomethyl)naphthalene, 4-(chloromethyl)biphenyl, and 2,2,2-trifluoroethyl trifluoromethanesulfonate[6] were unsuccessful.

N-Aryl derivatives of methyl isonicotinate (III) were prepared by treatment of the *N*-(2,4-dinitrophenyl) derivative of the ester (II) with the appropriate aromatic amine (the Zincke synthesis). The 2,4-dinitro ester (II) was prepared by action of 2,4-dinitrophenyl *p*-toluenesulfonate[7] on methyl isonicotinate as described. Subsequent conversions[8] to the desired *N*-aryl esters (III) were carried out by adding 0.8 mol of the dinitro reagent in methanol to a stirred solution of 1.0 mol of the appropriate aromatic amine in methanol over a period of 10 min. Immediately after the addition, the solution became dark red (indicating opening of the pyridine ring of the ester) but turned, within minutes, to a yellow color of the liberated dinitroaniline. Reaction mixtures were concentrated by removal of methanol under reduced pressure and then poured into excess ether, and the resulting



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[1] Support of this work by the National Science Foundation (Grant No. 8022881) is gratefully acknowledged.

[2] (a) Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1073. (b) Radlowski, C. A.; Chum, P.-W.; Hua, L.; Heh, J.; Gould, E. S. *Inorg. Chem.* **1980**, *19*, 401. (c) Singh, A. N.; Radlowski, C. A.; Reed, J. W.; Krishnamurthy, V. V.; Gould, E. S. *Ibid.* **1981**, *20*, 211.

[3] Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. In the procedure of these workers, the desired complex was precipitated from the reaction mixture by addition of saturated aqueous NaClO_4. An additional recrystallization from 0.1 to M HClO_4 was found here to give a superior product.

[4] (a) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2329. (b) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673.

[5] (a) Meyer, H. *Monatsh. Chem.* **1903**, *24*, 199. (b) Gould, E. S. Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 2243.

[6] Hansen, R. L. *J. Org. Chem.* **1965**, *30*, 4322.

[7] Bunnett, J. F.; Basser, J. Y. *J. Am. Chem. Soc.* **1959**, *81*, 2104.

[8] de Gee, A. J.; Sep, W. J.; Verhoeven, J. W.; deBoer, T. J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 676.

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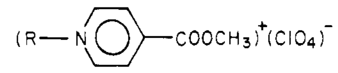
Table I. N-Substituted Isonicotinic Ester Perchlorates



R	% C[a]	% H[a]	% ClO_4[a,b]	λ_{max}, nm (ϵ[c])
phenyl (IV)	49.5	3.81	33.9	282 (16.8), 215[e] (24)
	(49.7)	(3.82)	(31.9)	
4-fluorophenyl (V)	46.8	3.21	31.2	284 (10.0), 215[e] (15)
	(47.0)	(3.31)	(30.1)	
1-naphthyl (VI)	56.1	3.70	27.6	363 (1.9), 318 (1.4), 311 (1.4),
	(56.0)	(3.58)	(27.5)	273 (12.3), 270 (11.9), 216 (140)
2-naphthyl (VII)	56.0	3.75		316 (9.1), 271 (21), 219 (100)
	(56.0)	(3.58)		
1-naphthylmethyl (VIII)	56.7	4.33	26.8	280 (10.5), 219 (200)
	(57.1)	(4.23)	(26.4)	
3-pyridyl (IX)	45.5	3.42	32.0	276 (12.0), 220[e] (13)
	(45.7)	(3.50)	(32.0)	
pentafluorobenzyl (X)[d]	38.5	1.80	24.9	262 (6.9), 212[e] (17)
	(38.6)	(1.73)	(24.8)	

[a] Calculated values in parentheses. [b] Reference 5b. [c] ϵ values in M^{-1} cm^{-1} $\times 10^{-3}$; solvent water. [d] N-substituted isonicotinic acid. [e] Shoulder.

precipitate was washed with ether. The precipitated tosylate salt was dissolved in water; the resultant solution was decolorized with charcoal and converted to the desired pyridinium perchlorate by addition of $HClO_4$. The latter salt was recrystallized from a dilute solution of $HClO_4$.[9] In our hands, the dinitro ester II failed to react with pentafluoroaniline, 2-fluoroaniline, and 2-aminobiphenyl. Reactions with 2- and 4-aminopyridine yielded intractable dye-like materials. Analyses of new N-substituted isonicotinoyl derivatives appear in Table I.

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at 475 nm, the low-energy Co(III) maximum, using a Cary Model 14 spectrophotometer as described.[2a,4] Reactions were carried out in 1.0 M $HClO_4$ with either Co(III) or Eu^{2+} in greater than fivefold excess. Reactions were first order in Eu^{2+} and very nearly first order in catalyst. With Eu^{2+} in excess, and Eu^{3+} added, kinetic traces resembled exponential decay curves (indicating an approach to first-order dependence on Co^{III}), but in a number of instances, appreciable distortion during the early portion of the reaction was observed. This distortion, which reflected the algebraic form of the catalytic rate law (see Results and Discussion), became negligible during the latter stages of reaction (as Co^{III} was consumed and additional Eu^{III} was generated). In such cases specific rates were evaluated from data taken during the last 50% reaction. In general, reactions were followed for at least 5 half-lives. Specific rates obtained from replicate runs agreed to within 10%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments. Catalytic attrition during a single kinetic run using excess reductant, as described for several of the most active catalysts,[2b,c] was negligible. Moreover, solutions of the *N*-benzyl-type catalysts retained their activity even after contact with 0.025 M Eu^{2+} for 20 min. The *N*-aryl-type catalysts were somewhat more fragile, losing approximately half of their activity after a 5-min treatment with this reductant.

The *N*-(3-pyridyl) derivative (IX) did not exhibit catalytic activity under our reaction conditions. In the presence of Eu^{2+}, it is rapidly reduced to a strongly absorbing yellow species (λ_{max} 377 nm, ϵ 1.0 $\times 10^3$ M^{-1} cm^{-1}) thought to be an aromatic radical analogous to those reported to be generated by reduction of pyrazine derivatives with Eu^{2+} and V^{2+}.[10] Like several known pyrazinyl radicals,[10b] this species decomposed rapidly in the medium used,[11] complicating attempted measurements of the specific rates at which it reduces substitution-inert cobalt(III) complexes.

Table II. Representative Kinetic Data for the Europium(II) Reduction of (Pyridine)pentaamminecobalt(III), $(NH_3)_5(py)Co^{3+}$, As Catalyzed by the *N*-Phenylisonicotinic Ester (IV)

$10^3[Co^{III}]$, M	$[Eu^{2+}]$, M	$10^6[cat]$, M	$[Eu^{3+}]$, M	10^2k,[a] s^{-1}
2.3	0.025	0	0	0.21[b]
2.3	0.025	2.6	0.050	1.39
2.3	0.025	5.2	0.050	2.7
2.3	0.025	7.8	0.050	3.9
2.3	0.025	10.4	0.050	5.3
2.3	0.035	2.6	0.050	2.2
2.3	0.025	2.6	0.080	1.51
2.3	0.050	2.6	0.050	2.9
17.0	0.0020	21	0	1.44
17.0	0.0020	42	0	3.2
17.0	0.0020	63	0	3.9
17.0	0.0020	84	0	5.3

[a] Pseudo-first-order rate constants at 25 °C. Reactions were carried out in 1.0 M $HClO_4$. [b] Reference 2a.

Results and Discussion

As in earlier studies,[2,12] catalysts are taken to operate through sequence (2), which leads, on application of the

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

$$\text{rate} = \frac{k_1k_2[Co^{III}][Eu^{2+}][\text{cat}]}{k_{-1}[Eu^{3+}] + k_2[Co^{III}]} + k_{un}[Co^{III}][Eu^{2+}] \qquad (3)$$

steady-state approximation to the radical "cat·", to rate law (3), in which the k_{un} term, pertaining to the uncatalyzed path, is very nearly negligible in these systems. The denominator in the first term of (3) reflects competition between Co^{III} and Eu^{3+} for the radical intermediate (cat·). With Co(III) in deficiency and with sufficient Eu^{3+} added, the k_{-1} term is dominant, leading to a catalyzed reaction that is first order in Co^{III} and inhibited by Eu^{3+}. With Co^{III} in large excess, rates become nearly independent of Co(III).[2a]

Representative kinetic data pertaining to the reaction catalyzed by the *N*-phenyl-substituted catalyst (IV) appear in Table II. When Co(III) is kept in deficiency, a plot of the pseudo-first-order specific rates vs. the expression [cat]-

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(9) The product derived from the reaction of 3-aminopyridine with ester II was precipitated with saturated $NaClO_4$ and was unusually soluble in water.

(10) (a) Chang, C.-R.; Paton, S. J.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1294. (b) Singh, A. N.; Balasubramanian, P. N.; Gould, E. S. *Ibid.* **1983**, *22*, 655.

(11) In 1.0 M $HClO_4$ at 25 °C, the radical derived from the *N*-(3-pyridyl) derivative disappears by a first-order path with a half-life period near 25 s.

(12) (a) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942. (b) Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1977**, *16*, 2516. (c) Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Ibid.* **1978**, *17*, 1142. (d) Srinivasan, V. S.; Radlowski, C. A.; Gould, E. S. *Ibid.* **1981**, *20*, 3172.

Table III. Composite Rates and Kinetic Parameters for Europium(II) Reductions of (Pyridine)pentaamminecobalt(III), As Catalyzed by N-Substituted Isonicotinic Esters and Related Derivatives

catalyst	k_1k_2/k_{-1}[a]	k_1	k_2/k_{-1}
isonicotinamide[b]	15.4	2.1	7.3
N-methylisonicotinic acid[b]	115	16	7.2
N-(carboxymethyl)isonicotinamide[c] (XI)	8.9×10^2	170	4.0
dimethyl 2,4-pyridinedicarboxylate[c]	2.5×10^4	1.6×10^3	16
N-benzylisonicotinic acid (XII)	9.0×10^2	73	12
N-(pentafluorobenzyl)isonicotinic acid (X)	3.3×10^3	4.6×10^2	7.2
N-(1-naphthylmethyl)isonicotinic ester (VIII)	1.3×10^3	1.1×10^2	12
N-phenylisonicotinic ester (IV)	9.0×10^3	5.8×10^2	16
N-(4-fluorophenyl)isonicotinic ester (V)	1.5×10^4	7.4×10^2	20
N-(1-naphthyl)isonicotinic ester (VI)	1.0×10^4	5.4×10^2	19
N-(2-naphthyl)isonicotinic ester (VII)	1.7×10^4	1.1×10^3	16
N-(3-pyridyl)isonicotinic ester (IX)	*d*		

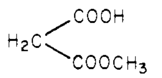
[a] Values of k_1 and the quotient k_1k_2/k_{-1} (see eq 2) are in $M^{-1}\ s^{-1}$. The ratio k_2/k_{-1} is dimensionless. Reactions were carried out in 1.0 M $HClO_4$ at 25 °C. [b] Reference 2a. [c] Corrected for severe catalyst deterioration during runs (see ref 2c). [d] Not catalytic.

$[Eu^{2+}][Eu^{3+}]^{-1}$ gives the quotient k_1k_2/k_{-1} as slope. With the oxidant in excess, plots of rate constants vs. [cat] yield values of k_1 as slopes. Individual values of k_2 and k_{-1} cannot be obtained from steady-state experiments alone.

Resulting kinetic parameters are assembled in Table III; values for several catalysts investigated in early work are also included for comparison. As with previous series,[2,12] in which the initial reduction of the catalyst is taken to proceed by an inner-sphere path,[13,14] there is relatively little variation in the ratio k_2/k_{-1}. Hence, the quotient k_1k_2/k_{-1}, which may be regarded as a measure of catalytic effectiveness under the usual conditions, is determined mainly by k_1.

We find values of k_1 to be unexpectedly sensitive to variation in the substituent bound to the ring nitrogen in the catalytic cation. Replacement of just one of the methyl hydrogens in the *N*-methyl catalyst by a phenyl group is seen to result in a fivefold increase in this rate constant. Since the two aromatic rings in the resulting *N*-benzyl derivative are separated by a methylene linkage ($^+N-CH_2-Ph$), there can be no conjugative interaction between them, and this acceleration must be attributed to electron withdrawal[15] by the phenyl group, an effect that may be further enhanced by substitution of five fluoro substituents for the phenyl hydrogens (X).

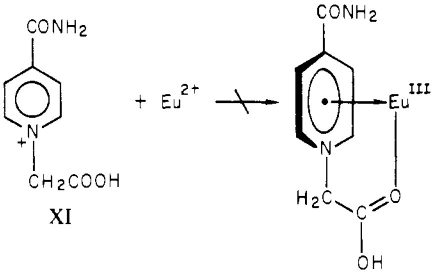
On this basis, the observation that the *N*-benzyl catalyst and its pentafluoro derivative (X) are no less effective than the *N*-carboxymethyl cation (XI) is in accord with the closely similar electron-attracting capabilities of the N-bound substituents, as reflected, for example, in the reported pK_A values of carboxylic acids XIII and XIV. At the same time, serious doubt is cast on the earlier suggestion[12d,20] that the radical derived from cation XI is stabilized by homoallylic interaction of type XV.[21]



XIII (pK_A 3.42[16,17])

$C_6F_5CH_2COOH$

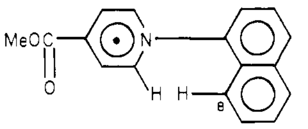
XIV (pK_A 3.48[18,19])



XI

XV

In catalysts IV–VII, the methylene bridge has been removed and the aryl group is attached directly to the ring nitrogen. Further improvement in catalytic effectiveness is seen to result, implying increased stabilization of the radical intermediate. We attribute this enhancement principally to generally stronger electron withdrawal from the pyridine system, rather than to the conjugative delocalization of the unpaired electron to alternating sites in the isocyclic ring. This view reflects the evaluations by Wepster and co-workers[15,22] of the relative importance of inductive electron withdrawal and conjugative in *N*-aryl systems, as well as the earlier report by Bastiansen[23] that the benzene rings in biphenyl (which is isosteric with the *N*-phenyl systems under consideration) are skewed, rather than coplanar in the vapor state. Note that in radical XVI, which is derived from the 1-naphthyl catalyst (VI), coplanarity between the two ring systems is further disfavored by strong nonbonded interaction between the α-hydrogen of the pyridine system and the hydrogen on the 8-position of naphthalene.



XVI

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[13] In all catalytic systems of this type, k_2 pertains to an outer-sphere process. When the initial (k_1) step and, by implication, its reversal (k_{-1}) are also outer sphere, the ratio k_2/k_{-1} is very nearly constant (3×10^3),[12b] in accordance with the model of Marcus.[14] This ratio is, however, much greater than the ratios calculated for the systems at hand.

[14] See, for example: Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[15] See, for example: Hoefnagel, A. J.; Hoefnagel, M. A.; Wepster, B. M. *J. Org. Chem.* **1981**, *46*, 4209.

[16] Brown, H. C.; McDaniel, D. C.; Hafliger, O. "Determination of Organic Structures by Physical Methods"; Braude, E. A., Nachod, F. C., Eds.; Academic Press: New York, 1955; Vol. 1, Chapter 14. In this instance pK_A for the monomethyl ester of malonic acid is cited, rather than that for the parent diacid, to eliminate statistical considerations, as well as complications arising from internal hydrogen bonding.[17] The electron-withdrawing properties of the $-CH_2COOH$ function are considered to resemble closely those of $-CH_2COOCH_3$.

[17] See, for example: Westheimer, F. H.; Benfey, O. T. *J. Am. Chem. Soc.* **1956**, *78*, 5309.

[18] Petrov, V. P.; Koptyug, V. A. *Reakts. Sposobn. Org. Soedin.* **1966**, *3*, 135; *Chem. Abstr.* **1967**, *66*, 108906*b*.

[19] Note that the γ-substituent on catalyst X is $-COOH$, whereas that on XI is $-CONH_2$. In related systems, this substitution has been found[2a] to increase catalyst effectiveness approximately tenfold.

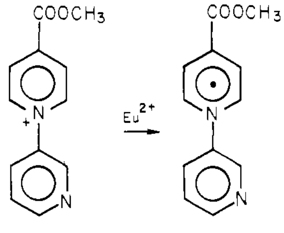
[20] Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.

[21] Analogous homoallylic interaction is not, however, ruled out for the rapid Cr^{2+} reduction of the $(NH_3)_5Co^{III}$ complex of XI. In this instance, the Cr(III) center in the oxidation product has been found to be bound to the carboxyl group.[20]

[22] (a) Wepster, B. M. *Recl. Trav. Chim. Pays-*Bas **1952**, *71*, 1159, 1171. (b) van der Krogt, S. M. H.; Wepster, B. M. *Ibid.* **1955**, *74*, 161.

[23] Bastiansen, O. *Acta Chem. Scand.* **1949**, *3*, 408. This worker reports the average "pivot angle" between the two bound benzene rings as 45 ± 10°.

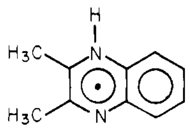
The 3-pyridyl-substituted cation (IX), which forms the most stable radical (XVII) in the present series, is catalytically inactive. In considering the catalytic sequence (2) for systems in which the radical intermediate, cat·, is present in small steady-state concentrations, Fanchiang[2a,12a] has pointed out that stabilization of the radical enhances the effectiveness of its parent catalyst by increasing the steady-state concentration of an active intermediate. At the same time, however, it is recognized that, under conditions where conversion to the radical becomes nearly complete, further stabilization retards its reactions with primary oxidants[24] without substantially increasing its available concentration. Radical XVII may be considered analogous to the substituted quinoxalinium radical XVIII with respect both to structure (the two radicals feature two ring nitrogens separated by a pair of aromatic carbons) and to spectral characteristics. Reaction of the latter species with $Co(NH_3)_5py^{3+}$ has also been shown to proceed immeasurably slowly.[10b]



IX

XVII

λ_{max} 377 nm



XVIII

λ_{max} 370 nm

Perhaps the most noteworthy feature of this study is the observed resistance of the catalysts in the group to attrition under conditions of use. Of the several very powerful catalysts previously described,[2bc,12a] all but one[12d] undergo such severe deterioration in Eu(II)–Co(III) systems that they become very nearly inactive after a single kinetic run. In contrast, catalysts in the present series exhibit no significant loss of activity during a single run with Eu^{2+} in large excess. Moreover, the *N*-benzyl catalysts suffer no apparent ill effects during use in several successive runs. The *N*-aryl-type catalysts (IV–VII), however, are significntly less robust.

Consideration of kinetic profiles of reactions carried out with rapidly deteriorating catalysts[2c] indicated that attrition occurs through a combination of disproportionation (eq 1) and overreduction (eq 4) of the radical intermediate. Since the first of these processes has been shown to be much more severe with nonalkylated than with N-alkylated catalysts,[2c] we suspect that it is initiated by the basic (ring deprotonated) form of the radical, although the net reaction ultimately consumes protons.

$$2\text{cat}\cdot \xrightarrow{2H^+} \text{cat} + \text{cat}H_2 \qquad (1)$$

$$\text{cat}\cdot + Eu^{2+} \xrightarrow{2H^+} \text{cat}H_2 + Eu^{3+} \qquad (4)$$

Overreduction may persist despite N-substitution, but its importance is seen to vary greatly as one catalyst is substituted for another. Detailed spectral studies[25] of pyridinyl radicals closely related to those intervening in the present series of reactions have led to the conclusion that these are partially and reversibly associated into dimeric species (π-mers) in both isopentane and acetonitrile. We thus cannot rule out the possibility that the radicals from the more robust catalysts are protected here by analogous association into dimers,[26] which are presumed to be less easily reduced than are the radicals themselves. Although marked differences in solvent polarity and in concentration levels obviously dictate caution in drawing this analogy, it may reasonably be argued that radical dimerization requiring π-interaction is significantly more important for the *N*-benzyl-type radicals than for the *N*-aryl in which the composite rings of the monomers are almost certainly skewed. In this regard, the recent observation[25b] that the presence of an N-bound *tert*-butyl group prevents "π-merization" of pyridyl radicals is of interest, for a bulky nonplanar substituent of the latter type would likewise be expected strongly to disfavor intermolecular attraction between ring faces.[27]

Registry No. IV, 86411-30-5; V, 86411-32-7; VI, 86411-34-9; VII, 86411-36-1; VIII, 86411-38-3; IX, 86411-40-7; X, 86421-58-1; XI, 78307-95-6; XII, 86411-42-9; $Co(NH_3)_5py^{3+}$, 75456-03-0; Eu, 7440-53-1.

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(24) Fanchiang, Y.-T.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 1827.

(25) (a) Itoh, N.; Nagakura, S. *J. Am. Chem. Soc.* **1967**, *89*, 3595. (b) Hermolin, J.; Levin, M.;Kosower, E. M. *Ibid.* **1981**, *103*, 4808.

(26) Note that involvement of the radical intermediate in a rapidly reversible monomer–dimer equilibrium will not alter our kinetic treatment of the catalytic systems. Calculations of the steady-state concentrations of the radicals in these systems will, however, be affected.

(27) A reviewer suggests the possibility that the proposed π-mer of two radicals may be reduced by Eu^{2+} more readily than the monomeric radical, rather than less so, and that both the *N*-benzyl and *N*-phenyl radicals are protected from dimerization simply by the bulk of their N-bound substituent. An earlier observation[2b] that nonalkylated isonicotinic acid derivatives (in contrast to pyridinedicarboxylato species) are among the most robust of the known electron-transfer catalysts appears to weigh against this suggestion.