

- (19) See, for example, E. F. Caldin, "Fast Reactions in Solution", Wiley, New York, N.Y., 1964, p 12.
- (20) For a view more closely corresponding to our own, see R. G. Linck, *MPT Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 903 (1971).
- (21) See, for example, R. L. Pecsok and N. Bjerrum, *Acta Chem. Scand.*, 11, 1419 (1957).
- (22) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 533, 550 (1964).
- (23) There is some evidence²² that Jahn-Teller distortion, to which octahedral complexes of Cu^{II} (and Cr^{III}) are subject, raises selectivity toward salicylate. This effect (approximately 1 pK unit) appears to be too small to alter the argument presented.

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

Electron Transfer through Organic Structures. 22. Mediation by Acylpyridines¹

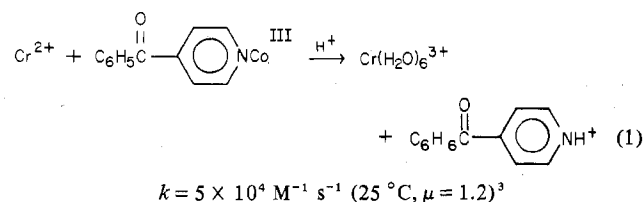
EDWIN S. GOULD,* NELSON A. JOHNSON, and ROBERT B. MORLAND

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The reductions of eight 3- and 4-acylpyridine derivatives of (NH₃)₅Co^{III} (IV, V) with Cr²⁺, Eu²⁺, and V²⁺ are compared. These complexes were prepared through the respective 1,3-dioxolanes (III). The acetyl, benzoyl, and butyryl derivatives exist in aqueous solution in the nonhydrated (carbonyl) forms, whereas the 3- and 4-CHO complexes are partially converted to hydrates (-CH(OH)₂). The ratios of specific rates for Cr²⁺ and V²⁺ reductions of the keto complexes lie in the range 10²-10⁴, in contrast to *k*_{Cr}/*k*_V ratios near 0.02 for reductions which are unequivocally outer sphere. Observed *k*_{Eu}/*k*_V ratios (10¹-10³) are likewise far greater than the characteristic outer-sphere ratios (0.3) for this pair of reductants. Arguments are presented that reductions of the keto complexes by Cr²⁺ and Eu²⁺ are predominantly inner sphere but that the two possible paths are of comparable magnitude with V²⁺. A plot of log *k*_{Cr} vs. log *k*_{Eu}, which includes values both for the keto complexes and for carboxylato complexes, approaches linearity, with the least-squares line corresponding to the equation log *k*_{Eu} = 0.61 log *k*_{Cr} + 0.36. This appears to be the first application of a linear free energy relationship to an inner-sphere series in which substantial structural variation occurs in the path of electron transfer. In the Cr²⁺ reactions with the -CHO complexes, a major fraction of each reduction occurs by a path independent of Cr²⁺ but first order in H⁺. For this component, the rate is determined by slow generation of the more reactive keto form of the oxidant from the less active hydrate. Reductions by V²⁺ exhibit only one kinetic component, for the interconversion between forms is rapid in comparison with the reduction of either form. Reduction of the 4-CHO complex by Cr²⁺ is further complicated by the very rapid secondary reaction of Cr²⁺ with 4-pyridinecarboxaldehyde, liberated in the primary reaction, to form a strongly absorbing species, the properties of which correspond to a Cr(III)-bound radical cation, VII. The latter undergoes aquation (*k* = 63 s⁻¹ at 25 °C) to a radical which, in turn, dimerizes to glycol IX, which can be isolated. The delay in formation of VII from the cobalt(III)-aldehyde complex points to a rate which is determined by aquation (*k* = 470 s⁻¹ at 25 °C) of the carbonyl-bound chromium(III) product, X, formed initially by the very rapid electron transfer between metal centers.

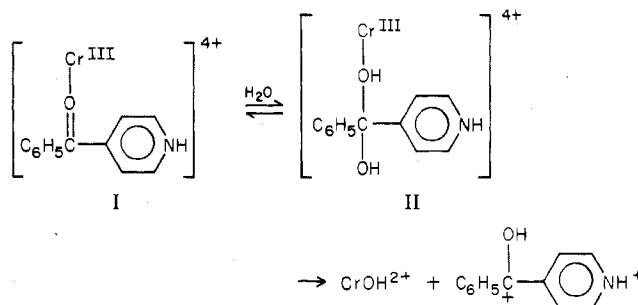
The reductions of cobalt(III) complexes of substituted pyridines have furnished several of the more instructive examples of dramatic rate changes resulting from minor structural alteration.² For instance, incorporation of a 4-benzoyl group in pyridinepentaamminecobalt(III) increases, by a factor of 10⁷, the specific rate of its reduction (eq 1) with



Cr²⁺.^{2b,c,3} The magnitude of this rate enhancement has been attributed to a change in mechanism; i.e., it has been proposed that in contrast to the pyridine complex, which must be reduced via an outer-sphere path, the benzoylpyridine derivative is reduced by attack of Cr²⁺ at the keto group. The latter bridged path should yield the Cr(III)-bound ketone, I, as a primary product, but spectral profiles of this reaction³ gave no indication of the intervention of such a species, although analogous intermediates of the type ^{III}Cr-O=CHAr have been detected in less strikingly accelerated reactions of a related type in which the aldehyde group assumes a "lead-in" role.³⁻⁵

Note that the proposed inner-sphere intermediate, I, features two aryl groups bound to the carbonyl carbon, whereas the aldehyde-bound intermediates have but one. It has long been recognized that the unimolecular heterolysis of C-O or C-X bonds in alkyl arenulfonates or halides may be accelerated by several orders of magnitude in polar solvents upon in-

corporation of an aromatic ring α to the reaction center.⁶ In somewhat the same way, heterolysis of the C-OCr bond in II, which is in mobile equilibrium with I,⁷ would be expected



to proceed much more rapidly than the corresponding conversion for the hydrates of the aldehyde intermediates, which exhibit decay constants near 10¹ s⁻¹ in water at 25 °C.^{3,4} A rate enhancement of 10³ is not unreasonable,⁶ leading to an estimated decay constant near 10⁴ s⁻¹ for the benzoyl intermediate I. Since the maximum degree of conversion to I under typical stop-flow experimental conditions would then be only a few percent and would occur before less than 10⁻³-s reaction time,⁸ it would almost certainly be missed.

The present work deals principally with carbonyl-substituted pyridinecobalt(III) derivatives having no second aryl group, several of which are reduced very nearly as rapidly as the 4-benzoyl complex. Although evidence for intervention of a carbonylchromium(III) intermediate is still not as clear-cut as desired, we have encountered some entertaining points. Moreover, there has been further development of synthetic procedures.

Table I. Pentaamminecobalt(III) Perchlorates, $\text{LCo}(\text{NH}_3)_5(\text{ClO}_4)_3$

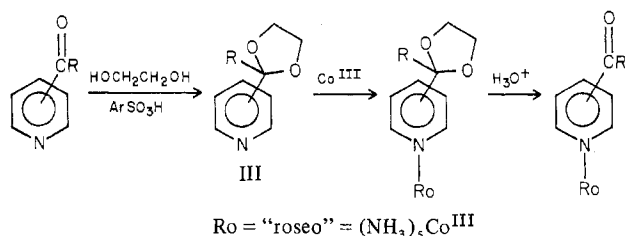
Organic ligand, L	Heating time, min (90 °C)	% calcd		% found ^a	
		C	H	C	H
3-Pyridinecarboxaldehyde (IV, R = H) ^b	15	13.0	3.62	13.0	3.70
4-Pyridinecarboxaldehyde (V, R = H) ^b	35	13.0	3.62	12.9	3.52
4-Acetylpyridine (V, R = CH ₃) ^b	45	14.8	3.88	15.0	4.03
4-Butyrylpyridine (V, R = <i>n</i> -C ₃ H ₇) ^b	30	18.2	4.39	18.1	4.26
4-(<i>p</i> -Chlorobenzoyl)pyridine (V, R = <i>p</i> -ClC ₆ H ₄) ^c	50	22.0	3.52	21.9	3.63
Pyrazine (VI)	40	9.17	3.63	8.98	3.64

^a Analyses by Galbraith Laboratories, Inc. ^b Carbonyl group protected by conversion to the 1,3-dioxolane during preparation of the Co(III) complex (see Experimental Section). ^c Prepared without protection of the carbonyl group.

Experimental Section

Materials. Solutions of Cr(II),^{2a} Eu(II),⁹ and V(II)¹⁰ were prepared and analyzed as described. Heterocyclic bases (Aldrich or Pfaltz and Bauer products) were used as received. Lithium perchlorate¹¹ and aquopentaamminecobalt(III) perchlorate^{2a} were prepared as described. The degree of success achieved in preparations using the latter perchlorate appeared to be strongly (and unaccountably) dependent on the exact manner in which it was purified. For best results, it was recrystallized by dissolving in 10 times its weight of water at 70 °C, carefully adding HClO₄ to the beginning of crystallization, reheating to dissolve the precipitate, and then cooling slowly to 0 °C. The crystals, which should have well-formed faces, were dried in air and powdered just before use.

Preparation of Cobalt(III) Complexes. Complexes were prepared by modifications of an earlier procedure,^{2c} in which aquopentaamminecobalt(III) perchlorate was heated with an excess of substituted pyridine in dimethylformamide. In the original treatment, ring-bound aldehyde groups and the 4-COCH₃ group suffered oxidation by Co(III); hence carbonyl functions were here protected by conversion to 1,3-dioxolanes (III)¹² before ligation



A mixture of 0.30 mol of the aldehyde or ketone, 0.39 mol of ethylene glycol, 0.32 mol of *p*-toluenesulfonic acid monohydrate, and 250 ml of benzene was refluxed in a 1000-ml flask fitted with a Dean Stark trap and condenser until all water was removed (3–12 h). The cooled solution was carefully neutralized with saturated Na₂CO₃, and the benzene layer was separated. The aqueous layer was extracted with two 300-ml portions of ether, the combined organic extracts were dried over anhydrous Na₂SO₄, and the solvents were removed under rotary evaporation. The remaining crude dioxolane was then distilled at reduced pressure.

For conversion to the ring-bound (NH₃)₅Co^{III} derivative, 2.0 g of the powdered aquo perchlorate was converted to the DMF complex by treatment with 3 ml of dimethylformamide at 95 °C. To the resulting slurry was added 3.0 g of the dioxolane, and the mixture was heated at 90 °C while stirring was maintained. Heating times are listed in Table I. As conversion proceeded, the rose color in solution changed to a deep orange. The mixture was then cooled and extracted with two 100-ml portions of ether, and the ether extracts were discarded. To the pasty material remaining was added 50 ml of hot methanol. The mixture was cooled and filtered to remove the unreacted DMF complex. The filtrate was concentrated to 20 ml by rotary evaporation, and 15 ml of a saturated methanolic solution of NaI was added, slowly precipitating the cobalt(III)-dioxolane complex as its iodide. The mixture was cooled to -15 °C, and the yellow iodide was filtered off, washed with cold ethanol and then with ether, and immediately recrystallized from a minimum volume of water at 70 °C. The recrystallized iodide was redissolved in water and then converted to the perchlorate by passage through an anion-exchange column (AG2-X8, Bio-Rad, 200–400 mesh) in the perchlorate form. To the eluent was added 1.0 ml of concentrated HClO₄, remaining traces of iodide were removed by dropwise addition of dilute AgClO₄,

and the excess silver ion was precipitated by dropwise addition of concentrated HCl. The preparation was filtered and then concentrated to the onset of crystallization by rotary evaporation. Complete hydrolysis of the dioxolane to the parent carbonyl compound occurred during the evaporation of the acidic solution. The preparation was slowly cooled to 0 °C, and the yellow crystalline perchlorate was filtered off, washed with cold ethanol and with ether, and then dried in vacuo.

The dioxolane route may be applied not only to formyl and acetyl derivatives but also to the complexes of 3- and 4-benzoylpyridine, which have been prepared from the ketones.^{2c} The slight improvement in yield of the benzoyl complexes does not justify the extra time required for preparation of the dioxolanes. Attempted conversion of the dioxolane derived from 2-pyridinecarboxaldehyde¹³ to its cobalt(III) complex was not successful.

Increased yields and greater convenience were often achieved by substituting *N,N*-diethylacetamide for DMF as the reaction medium. The aquo perchlorate, if properly purified, dissolved completely in the acetamide, and the reaction mixture generally remained homogeneous during conversion to the pyridine complex. In such cases, precipitation and recrystallization of the triiodide (which is both photosensitive and heat sensitive) were by-passed, and the desired complex was precipitated, after the usual extraction with ether, by addition of equal volumes of water and saturated NaClO₄.

Analyses of complexes prepared here for the first time are given in Table I.

Kinetic Experiments. Specific rates were estimated from measurements of absorbance changes using the Durrum-Gibson stopped-flow spectrophotometer as described.³ Most measurements were made at 475 nm. Reactions of the keto derivatives were first order each in Co(III) and in reductant, but rate measurements employed pseudo-first-order conditions. The reductant was generally in greater than tenfold excess, but reduction of the pyrazine complex with Cr(II) was carried out with the oxidant in excess, for rapid secondary reactions yielding deeply colored products occur with excess Cr(II).^{9b} Except as noted below, rates were very nearly independent of acidity in the range 0.12–1.20 M H⁺. Ionic strengths were adjusted (in most cases to near 1.2 M) by addition of two times recrystallized LiClO₄. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments. Replicate reactions, with the same pair of master solutions, were carried out until absorbance curves for three consecutive runs superimposed. With reductions by Cr²⁺ and V²⁺, rate constants, obtained from logarithmic plots of absorbance differences against reaction time, agreed to better than 5% for runs with different master solutions, provided that half-life periods were 10 ms or greater. For faster reactions, instrument noise was more troublesome and reproducibility between runs accordingly less. Rate constants for reactions having half-life periods less than 1 ms could not be estimated reliably. Reductions with Eu²⁺ were extremely capricious; autocatalysis similar to that reported with related systems¹⁴ was frequently observed, and even when good first-order curves were obtained, reproducibility between runs was often poor. Satisfactory rate constants with this reagent were obtained only in a few cases.

Neither the 3- nor the 4-carboxaldehyde derivative gave a simple rate curve when reduced with excess Cr²⁺. In addition to absorbance changes occurring during the first few milliseconds after mixing, the two aldehyde derivatives exhibited a much slower kinetic component, corresponding to disappearance of a major fraction of the Co(III), with half-lives in the range 1–10 s. With both oxidants, the pseudo-first-order specific rate for this component was independent of [Cr²⁺] but strongly dependent on [H⁺]. Other evidence (see Results and Discussion), in addition to a marked similarity to the behavior

Table II. Yields of Co(II) from Reduction of Substituted Pentaamminecobalt(III) Complexes with Cr(II), V(II), and Eu(II)^a

Organic ligand	Yield of Co(II), %		
	Cr ^{II}	V ^{II}	Eu ^{II}
4-Benzoylpyridine	99	90	49
3-Benzoylpyridine	100 ^b	100	82
4-Acetylpyridine	100	90	50
3-Acetylpyridine	100 ^b	82	72
4-Pyridinecarboxaldehyde	52	82	51
3-Pyridinecarboxaldehyde	91	98	78
Pyrazine	100	88	

^a [H⁺] = 1.2 M; [Co(III)] = 0.020 M; [reductant] = 0.015 M; reductant was added to Co(III). ^b Reference 2c. [H⁺] = 0.12 M.

previously observed¹⁵ during the Cr(II) reduction of the glyoxalato derivative of (NH₃)₅Co^{III}, indicates that this component arises from conversion of the less active hydrated (-CH(OH)₂) form of the aldehyde to the much more reactive carbonyl form. Since this reaction was not of primary interest in the present study, it was not investigated in detail. Preliminary data are consistent with a specific rate 0.93[H⁺] s⁻¹ (25 °C, μ = 1.2) for dehydration of the 4-aldehyde complex and 2.0[H⁺] s⁻¹ (25 °C, μ = 0.24) for dehydration of the 3 isomer.

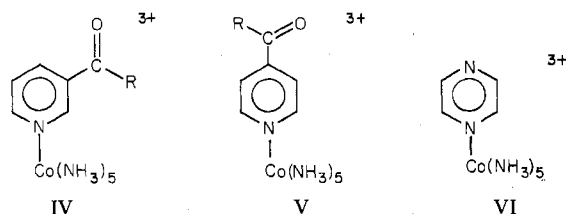
The more rapid absorbance change observed with the 3-CHO derivative corresponded, as expected, to a reaction first order each in Co^{III} and Cr²⁺, with a rate independent of acidity. Absorbance curves for the reaction of the 4-CHO complex featured a very sharp rise in absorbance in the region 400–480 nm and then a fall. The maximum absorbance occurred at 0.005 s, and the reaction curve at 440 nm, at which wavelength the transient species absorbed much more strongly than either reactants or products, could be shown⁸ to be a superposition of two first-order reactions with rate constants 470 and 63 s⁻¹. Neither of these values was dependent on [Cr²⁺] (within the range 0.005–0.02 M) nor on acidity (within the range 0.12–1.2 M). The absorption maximum of the intermediate species was found to lie near 447 nm (ε 8 × 10³).^{16,17} An intermediate having the same spectral and decay properties was observed when uncomplexed 4-pyridinecarboxaldehyde was treated with Cr²⁺, but under these conditions, its formation was complete within the time of mixing.

Additional Experiments. Stoichiometry experiments,^{2a} in which cobalt(III) and a ligand bound to it were allowed to compete for a deficient quantity of added reducing agent, were carried out by adding 0.015 mmol of reductant to 0.02 mmol of each of the several complexes (Table II) in 1.0 ml of 1.2 M HClO₄, using vials sealed by rubber serum caps. After these mixtures had been allowed to react for 10 min, the quantity of Co²⁺ formed was estimated as described.^{2a}

The reaction of uncomplexed 4-pyridinecarboxaldehyde with Cr²⁺ was carried out on a preparative scale. To 400 mg (3.7 mmol) of the aldehyde in 2.0 ml of distilled water was added 4.0 ml of a solution 0.94 M in Cr²⁺ and 1.0 M in HClO₄. The reaction mixture was kept under N₂ for 15 min and then neutralized with saturated Na₂CO₃. The preparation was boiled for a few minutes to coagulate the precipitated Cr(OH)₃; the mixture was filtered hot, and the filtrate was allowed to cool to 0 °C. The needlelike crystals (320 mg, 80%) obtained melted at 177 °C and did not depress the melting point of an authentic sample of *d,l*-1,2-bis(4-pyridyl)-1,2-ethanediol prepared from the bimolecular reduction of the aldehyde with zinc dust as described by Mathes and co-workers.¹⁸

Results and Discussion

Carbonyl-Hydrate Equilibria. The keto complexes in the present study would be expected¹⁹ to exist in aqueous solution virtually completely in the nonhydrated forms (IV, V), and



this is confirmed by the reduction behavior previously observed for the acetyl and benzoyl derivatives.^{2c} In contrast, substantial conversion of the aldehyde derivatives to their hydrated

Table III. Hydration of Pyridinecarboxaldehyde Derivatives^a

Aldehyde	δ _{CHO} ^b	δ _{CH(OH)₂} ^b	f _{CHO} ^c
4-Aldehyde, D ₂ O	9.82	5.82	0.68
4-Aldehyde, D ₂ O + DCl ^d		6.23	<0.02
3-Aldehyde, D ₂ O	9.80	5.95	0.89
3-Aldehyde, D ₂ O + DCl ^e	10.13	6.20	0.18
4-Aldehyde, (NH ₃) ₅ Co ^{III}	10.13	6.13	0.09
complex			
3-Aldehyde, (NH ₃) ₅ Co ^{III}	10.00	6.12	0.46
complex			0.50 ^f

^a NMR data in D₂O, 25 °C. ^b Values in relation to external TMS. ^c Mole fraction of aldehyde. ^d pD 1.71; see ref 20. ^e 20% DCl in D₂O. ^f Estimated from the relative magnitudes of the absorbance changes at 475 nm for the two-component kinetic curve obtained in the reduction by Cr²⁺.

-CH(OH)₂ forms occurs in aqueous media. NMR studies by Pocker and co-workers²⁰ show that the extent of hydration of 4-pyridinecarboxaldehyde may be markedly increased by acidification, and analogous measurements (Table III) point to a similar shift in equilibrium with the 3-aldehyde as well. The (NH₃)₅Co^{III} complex of the 4-aldehyde exists over 90% as the hydrate, whereas for the complex of the 3-aldehyde, in which the donor center and the aldehyde function are out of conjugation, the distribution between forms is less one-sided. The aldehyde-hydrate equilibria for the cobalt complexes appear to be independent of acidity in the pH range 0–7, for the spectra of these derivatives between 230 and 290 nm, known to be strongly affected by shifts in this equilibrium,²⁰ are here found to be virtually the same in 0.1 M NaClO₄ as in 0.1 M HClO₄. This equilibrium comes into play in the present study, for carbonyl-substituted pyridine complexes are reduced rapidly^{2c} whereas those with saturated side chains are generally reduced more slowly.²¹

Reductions of the Keto Complexes. A second complication in this work is the possibility that the reducible ligand may consume a portion of the reducing agent added. It has been shown previously^{2c} that acetyl- and benzoylpyridines are reduced readily by Cr²⁺, but the quantitative yields of Co²⁺ here obtained when the (NH₃)₅Co^{III} derivatives of these ligands are reduced with a deficiency of Cr²⁺ (Table II) show that the keto ligands do not compete effectively with their cobalt(III) complexes for this reductant. In contrast, the Cr²⁺ reduction of the 4-CHO complex yields only 0.5 equiv of Co²⁺ per Cr²⁺ consumed, indicating the occurrence of a rapid reaction of Cr²⁺ with the free ligand, consuming one electron per aldehyde molecule.

Similar rapid one-electron reductions of the liberated ligands appear to accompany the Eu²⁺ reductions of the 4-carbonyl complexes, for which yields of Co²⁺ lie very near 50%; this side reaction becomes relatively less important with the poorly conjugated 3 complexes. Ligand reduction in itself should not invalidate the specific rates measured with Eu²⁺ since kinetic studies were carried out with a large excess of reductant and intermediates or products absorbing appreciably near the Co(III) peak were not formed. However, strong autocatalysis linked to one-electron ligand reduction has been demonstrated in systems similar to these,^{9b,14a} and we have observed it in some of our Eu²⁺ reductions as well, although in other instances the autocatalytic component is negligible in relation to the primary reaction. There is no evidence that the slight, but unmistakable, departures from 1:1 stoichiometry observed in the V²⁺ reactions affect the reliability of the rate constants measured with this reductant in large excess.^{22,23}

Specific rates for reduction by Cr²⁺, V²⁺, and Eu²⁺ (values of *k*_{Cr}, *k*_V, and *k*_{Eu}) are summarized in Table IV. The *k*_{Cr}/*k*_V ratios (10²–10⁴) contrast markedly with those ratios (near 0.02) observed for reductions which are unequivocally outer sphere,^{10a} and the *k*_{Eu}/*k*_V ratios (10–10³) are likewise far in

Table IV. Reductions of Acylpyridine Derivatives of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ with Cr^{2+} , V^{2+} , and Eu^{2+} ^a

Ring substituent	k_{Cr}	k_{V}	k_{Eu}
3-Acetyl (IV, R = CH ₃)	135 54 ^b	1.68	
4-Acetyl (V, R = CH ₃)	9.7×10^4 8.7×10^4 ^b	4.6	5.7×10^2 4.1×10^2 ^b
4-Butyryl (V, R = <i>n</i> -C ₃ H ₇)	2.4×10^4	2.8	1.7×10^2 ^c
3-Benzoyl (IV, R = C ₆ H ₅)	2.4×10^2	3.7	20
4-Benzoyl (V, R = C ₆ H ₅)	4.8×10^4 2.5×10^4 ^b	3.0	1.9×10^3 1.4×10^3 ^b
4- <i>p</i> -Chlorobenzoyl (V, R = 4-ClC ₆ H ₄)	5.2×10^4	3.0	3.2×10^3
3-Aldehyde (IV, R = H)	1.6×10^4 ^{b, d}	3.4	
4-Aldehyde (V, R = H)	$>10^6$ ^e	1.43	
Pyrazine (VI)	1.0×10^5 ^b	7	

^a Specific rates are in $\text{M}^{-1} \text{s}^{-1}$ at 25 °C. $[\text{H}^+] = 0.12\text{--}0.60 \text{ M}$, $[\text{Co}^{\text{III}}] = 0.001$, $[\text{reductant}] = 0.005\text{--}0.20 \text{ M}$, $\mu = 1.20$ (unless otherwise indicated), and supporting electrolyte is LiClO_4 . ^b $\mu = 0.24$. ^c Slight autocatalysis; k was estimated from initial rate. ^d Value for the nonhydrated (carbonyl) form. Conversion to this form from the hydrated ($-\text{CH}(\text{OH})_2$) species proceeds at a specific rate of $2.0[\text{H}^+] \text{ s}^{-1}$ at 25 °C. ^e Lower limit for the nonhydrated (carbonyl) form. Conversion from the hydrated species proceeds at a specific rate of $0.93[\text{H}^+] \text{ s}^{-1}$ at 25 °C.

excess of the corresponding outer-sphere ratios (near 0.3) for this pair of reductants.^{9b} Deviations of this magnitude may be taken as strong evidence that the faster reductant in each pair is operating mainly through an inner-sphere path but leave in doubt the mechanism(s) used by the slower.

A more quantitative, but still approximate, picture may be obtained by considering reductions by $\text{Ru}(\text{NH}_3)_6^{2+}$ (very nearly always an outer-sphere reagent)²⁴ in conjunction with linear free energy relationships which have been shown^{9b} to correlate outer-sphere reductions of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ derivatives by dipositive metal centers. Fan^{9b} has reported a k_{Ru} value of $4.5 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 0.50$) for the 4-benzoyl complex in this series, and specific rates for the other keto derivatives should not be greatly different from this. From Fan's equations we may calculate outer-sphere components for the reduction of the 4-benzoyl complex to be 0.027 for Cr^{2+} , 0.51 for Eu^{2+} , and $1.5 \text{ M}^{-1} \text{ s}^{-1}$ for V^{2+} . The first two of these are very small fractions of the observed specific rates, but the calculated value for V^{2+} is 50% of the observed k_{V} . Thus, although the rate constant for V^{2+} is, in itself, consistent with a reduction which is predominantly inner sphere,^{10a} it now appears that the two possible V(II) paths are of comparable magnitude for the 4-benzoyl derivative and, very likely, for other 4-keto complexes in the present series as well.

Although linear free energy relationships have been found to correlate specific rates for outer-sphere redox series,^{24,25} as well as those for inner-sphere reactions in which the bridging path is kept constant while nonbridging ligands^{10b,26} or pendant groups on the mediating ligand^{9a,10a} are altered, they have not yet been applied to inner-sphere series in which structural variation occurs in the path of electron transfer. A log-log plot (Figure 1), which includes not only the k_{Cr} and k_{Eu} for the keto complexes, but also the corresponding values for the carboxylato complexes reported previously,^{9a} approaches linearity with the least-squares line corresponding to the equation $\log k_{\text{Eu}} = 0.61 \log k_{\text{Cr}} + 0.36$. As expected, the scatter in this plot is more severe (correlation coefficient 0.930) than that for the carboxylato complexes alone (0.986). However, when it is considered that the entries in the combined plot feature, as electron-transfer paths, the carboxyl group (a three-atom chain), a 3-ketopyridine (a five-atom path), and several 4-ketopyridines (with six-atom paths), it is perhaps astonishing that there is any measure of correlation at all.

The principal limitation of this treatment is apparent in the case of the pyrazine complex, VI, for which k_{Cr} is greatest in

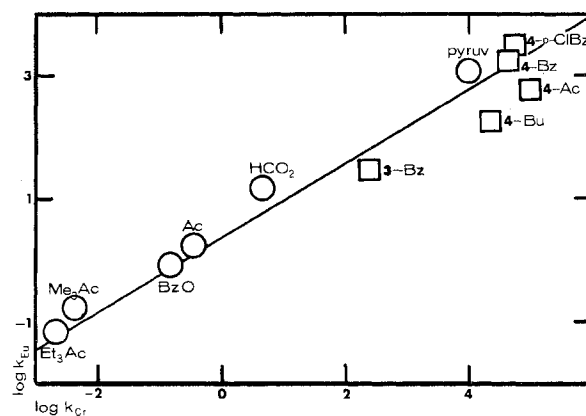


Figure 1. Log-log plot comparing the specific rates of reductions of pentaamminecobalt(III) complexes, $\text{R}(\text{NH}_3)_5\text{Co}^{\text{III}}$, by Cr^{2+} and Eu^{2+} (25 °C, $\mu = 1.0$). Oxidants include both carboxylato (\circ) and N-coordinated pyridine (\square) complexes. The least-squares line shown corresponds to the equation $\log k_{\text{Eu}} = 0.61 \log k_{\text{Cr}} + 0.36$ with a correlation coefficient 0.930.

the present series but k_{Eu} is least. Here the inner-sphere path has been further modified by substitution of nitrogen for oxygen as the lead-in atom. Earlier work has shown that mediating ligands featuring nitrogen and sulfur donors are much less effective redox bridges than those with donor oxygen for reductions with the hard reducing centers, $\text{Eu}(\text{II})^9$ and $\text{Ti}(\text{III})$,²⁷ whereas the reverse is true for the softer reductants, $\text{Cr}(\text{II})$ ²³ and $\text{Cu}(\text{I})$.¹¹ There is, at present, no substantial evidence for an inner-sphere path in the reduction, by Eu^{2+} , of N-bound pyrazine complexes.

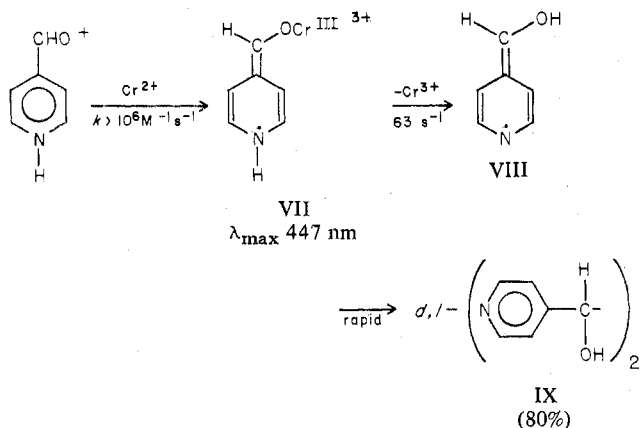
Reductions of the Aldehyde Derivatives. The two-component kinetic curve observed for the Cr^{2+} reduction of the 3-CHO complex is consistent with the NMR spectrum of this derivative in aqueous solution (Table III), which indicates partition into nearly equal quantities of a reactive carbonyl form and a much less reactive $-\text{CH}(\text{OH})_2$ form. From the faster component, we estimate the specific rate for reduction of the carbonyl form to be $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (25 °C, $\mu = 0.24$), almost 10^2 as great as the value for the closely related 3-COC₆H₅ complex. No convincing explanation of the greater mediating capability of the CHO group has yet appeared, although the effect has been already noted in the benzoato-cobalt(III) series.²⁸

The second kinetic component, although it requires Cr^{2+} , is zero order in reductant in the range 0.004–0.02 M Cr^{2+} and very nearly first order in H^+ . It is not observed in cases where $\text{Co}(\text{III})$ is taken in greater than twofold excess. This portion of the reaction brings to mind the Cr^{2+} reduction of the glyoxylato derivative of $(\text{NH}_3)_5\text{Co}^{\text{III}}$, in which an aldehyde group in conjugation with $-\text{COOCo}^{\text{III}}$ is, in aqueous solution, likewise partitioned into a very reactive carbonyl and a less reactive hydrated form.¹⁵ This carboxylato complex is reduced at a rate nearly independent of $[\text{Cr}^{2+}]$ at high concentrations of reductant. Under such conditions, the rate of reduction is determined by the rate of dehydration of the hydrate, a conversion strongly catalyzed by H^+ , for which the specific rate (25 °C) has been reported as $0.075 + 0.64[\text{H}^+] \text{ s}^{-1}$. The rate constant here estimated for the corresponding dehydration of the 3-pyridinecarboxaldehyde complex, $2.0[\text{H}^+] \text{ s}^{-1}$, is comparable both to that for the acid-catalyzed glyoxalato term and to that reported by Strehlow for the acid-catalyzed dehydration of pyruvic acid hydrate ($1.25[\text{H}^+] \text{ s}^{-1}$).^{29,30} A similar interpretation is applicable to the final (Cr^{2+} -independent) kinetic component in the reduction of the 4-CHO complex, for which a specific rate $0.93[\text{H}^+] \text{ s}^{-1}$ is here estimated. Additional measurements, particularly at lower acidities, are needed to establish the presence or absence of

a H^+ -independent term for the dehydrations of these aldehyde complexes.

Note that the reductions of these same complexes with V^{2+} are more straightforward, featuring single component curves, a first-order dependence on V^{2+} , and no significant acid dependence in the range 0.24–1.20 M H^+ . Although different specific rates would again be anticipated for the $-CH(OH)_2$ and $-CHO$ forms, both are reduced slowly in comparison to the interconversion between them in the acidic solutions used, and the measured specific rates (Table IV) may be taken as weighted averages of the rate constants for the two individual forms. The low k_V for the 4-CHO complex undoubtedly reflects the predominance of the less reactive hydrate in solutions of this oxidant.^{31,32} Partial resolution of these reductions into hydrate and aldehyde components is, in principle, possible at lower acidities.

Aside from the aldehyde-hydrate equilibrium, the Cr^{2+} reduction of the 4-CHO derivative is further complicated, in its early stages, by the growth and decay of a strongly absorbing intermediate. A species having the same absorption maximum (447 nm) and decay constant (63 s^{-1} at 25°C) as this intermediate is formed very rapidly (over 99% complete within 2 ms) when 10^{-3} M solutions of the uncomplexed aldehyde and Cr^{2+} are mixed in the stopped-flow chamber. The latter reaction is a one-electron reduction of the aldehyde, for when it is carried out on a preparative scale, the bimolecular reduction product, *d,l*-1,2-bis(4-pyridyl)-1,2-ethanediol (IX), is obtained in good yield. The strongly absorbing intermediate is then taken as a Cr(III)-bound radical cation, VII, and its observed decay, which is uni- rather than bimolecular, is attributed to aquation to radical VIII.

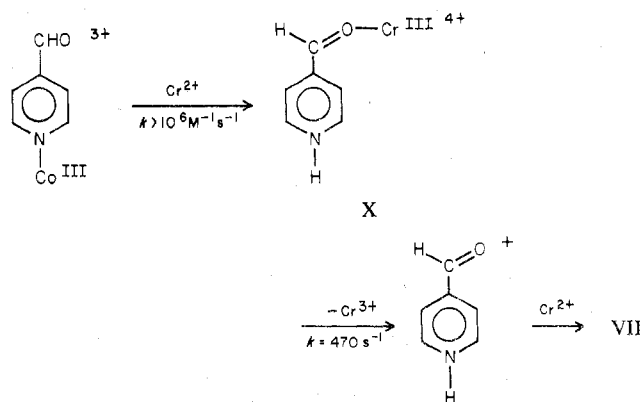


The radical cation is represented as O coordinated rather than N bound in consideration of its perceived lability.

The formation and loss of VII are noted only during the initial 0.04 s of the reaction of the cobalt(III)-aldehyde complex, for there is a rapid release of aldehyde shortly after mixing, resulting from reduction of the 9% of the complex present in the active (nonhydrated) form. Beyond this point, release of further ligand is governed by the relatively slow dehydration step, and changes in the very small concentration of VII become obscured by the absorbance changes reflecting the reduction of Co(III). However, throughout the reaction, virtually every act of reduction of Co(III) is followed by reduction of the ligand, for only 0.5 equiv of Co^{2+} is formed when 1 equiv of Cr^{2+} reacts with excess complex (Table II).

The formation of intermediate VII from the Co(III) complex of the 4-aldehyde is rapid, but its rate is measurable. Analysis of the reaction profile at 400 nm yields a specific rate $4.7 \times 10^2\text{ s}^{-1}$ for formation of VII by a process independent of $[Cr^{2+}]$. Since production of VII from the uncomplexed ligand has been found to be immeasurably rapid on our time scale, we must infer that the release of ligand is being delayed

here by a preliminary step, i.e., by the electron transfer between metal centers or by the destruction of the primary Cr(III) product, X. The electron transfer would be first rather than



zero order in $[Cr^{2+}]$; our observations are then consistent only with a delay arising from unimolecular aquation of X. Thus, although the present experiments detect neither the formation nor the decay of the primary Cr(III) intermediate X directly, they measure, if the proposed scheme be correct, the rate of a reaction governed by the decay.³³ The specific rate assigned to the aquation of the intermediate X is about 20 times that reported by Zanella⁴ for the aldehyde-bound Cr(III) derivative of 4-carboxybenzaldehyde, a difference which is related, at least in part, to the additional unit of positive charge associated with the protonated pyridine derivative.

It is likely that the chromium(III)-carbonyl product derived from the 3-CHO complex decays slightly more rapidly than its analogue X, for the positive nitrogen is closer to the Cr(III) center. It is, however, formed at a much lower specific rate (Table IV). Taking into consideration the distribution of the Co(III) complex of the 3-aldehyde between hydrate and carbonyl forms at the time of mixing (Table III), the maximum conversion to the 3 analogue of X may be calculated⁸ to be less than 10% and would occur 0.002–0.003 s after mixing. Hence it could easily be overlooked in our experiments, as would the 4-CHO-Cr(III) product were the latter not converted to a highly colored species. The carbonyl-bound Cr(III) intermediates in reduction of the keto complexes should undergo aquation even more rapidly (by a factor of $10-10^3$) than the aldehyde analogues and would be even more elusive. Such aquation, which may be presumed to involve C–O bond breakage,³⁴ cannot enter the picture in Cr^{2+} reduction of the pyrazine complex, VI. With Co(III) in excess, this very rapid reaction exhibits a single kinetic component, and earlier studies with derivatives of substituted pyrazines^{9b} show the primary Cr(III) product in such reactions to be N bound to the pyrazine ring.

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Registry No. IV (R = CH_3), 46422-63-3; IV (R = C_6H_5), 47087-22-9; IV(ClO_4)₃ (R = H), 59389-46-7; V(ClO_4)₃ (R = CH_3), 59389-48-9; V(ClO_4)₃ (R = *n*- C_3H_7), 59389-50-3; V (R = C_6H_5), 42582-66-1; V(ClO_4)₃ (R = 4- ClC_6H_4), 59389-52-5; V(ClO_4)₃ (R = H), 59389-54-7; VI(ClO_4)₃, 59389-56-9; Cr^{2+} , 22541-79-3; V^{2+} , 15121-26-3; Eu^{2+} , 16910-54-6; aquopentaamminecobalt(III) perchlorate, 14403-82-8.

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- (17) An additional kinetic component, a first-order decrease in absorbance, was observed for many Cr(II) reductions in this series when the mixtures were observed in the spectral range 300–330 nm. The decay constant, $3.5 \times 10^2 \text{ s}^{-1}$, was independent of $[\text{Cr}^{2+}]$, $[\text{H}^+]$, and $[\text{Co}^{\text{III}}]_0$. The magnitude of the spectral change could be minimized by taking special precautions to remove oxygen, but vestiges of the curve (with decay constant unchanged) persisted. The characteristics of this reaction are consistent with unimolecular decay of a complex formed very rapidly from the reaction of Cr(II) with traces of oxygen in the system (see, for example, M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959)).
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- (31) It is likely that the V^{2+} reduction of the 4-CHO derivative is predominantly outer sphere. The k_v value for this complex lies very close to that for the $(\text{NH}_3)_5\text{Co}^{\text{III}}$ complex of *N,N*-dimethylnicotinamide (1.38 s^{-1}),^{10a} an outer-sphere oxidant.³²
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- (33) The lower limit $10^6 \text{ M}^{-1} \text{ s}^{-1}$ for Cr^{2+} reduction of the 4-CHO complex was estimated by assuming the specific rate for this reduction (a pseudo-first-order reaction under the conditions used) to be at least 5 times that for aquation of X at the lowest concentration of Cr^{2+} taken (0.0025 M) to accommodate the observed nondependence on $[\text{Cr}^{2+}]$.
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Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer through Organic Structures. 23. Titanium(III) Reductions of Salicylatocobalt(III) Derivatives¹

ALBERT H. MARTIN and EDWIN S. GOULD*

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Rates of reduction, with Ti(III), of the salicylato (I) and several substituted salicylato derivatives of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ have been measured at 25 °C and 0.025–1.0 M H^+ in *p*-toluenesulfonate media. These reactions follow a rate law of the type: rate = $[\text{Ti}^{\text{III}}][\text{Co}^{\text{III}}]k_{\text{lim}}(1 + [\text{H}^+]/K)^{-1}$ where values of k_{lim} , the limiting specific rate at low acidities, lie near $100 \text{ M}^{-1} \text{ s}^{-1}$ and K is approximately 1 M. Neither the oxidant ($\text{p}K_{\text{A}} = 8\text{--}10$) nor the reductant ($\text{p}K_{\text{A}} = 2\text{--}3$) is substantially deprotonated in the region where $[\text{H}^+]$ dependence is steepest. Rate behavior is consistent with the intervention of a chelated precursor complex (II) formed (k_1) from the two metal centers with loss of H^+ , after which internal electron transfer (k_2) competes with nonproductive dissociation of the precursor (k_{-1}). Values of k_1 , which reflect substitution at the Ti(III) center, are comparable to reported estimates for $(\text{NH}_3)_5\text{CoF}^{2+}$ and $(\text{NH}_3)_5\text{CoN}_3^{2+}$ but about 10^2 lower than the specific rate for substitution of NCS^- at $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, which is electrostatically more favorable. The ratios k_2/k_{-1} for the salicylato oxidants are 20–100 times as great as for the fluoro and azido complexes, mirroring the enhanced stability of the salicylato precursor arising from chelation.

Since 1973 there has been a quickening of interest in the electron-transfer reactions of Ti(III).^{2,3} Various difficulties reported by earlier workers⁴ to be associated with choice of reaction media have been sidestepped, and specific rates for reduction of over two dozen Co(III) complexes by this d^1 center have been measured. Strong, although indirect, evi-

dence is at hand that such reactions proceed by inner-sphere paths if the oxidant features a sufficiently hard bridging ligand. It has further been shown^{3d} that chelating substituents having O donors may strongly influence reaction rates and that reaction paths featuring the loss of H^+ from the Ti(III) center are unusually prominent. Moreover, it now appears that