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Electron Transfer. 135. Pendant Carbonyl Groups in the Mediation of the Reactions of Indium(I) with Bound Ruthenium(III)[1]

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Reductions, using In^{I}(aq) and Ti^{III}(aq), of $(NH_3)_5Ru^{III}$ derivatives of pyridines having carbonyl-bearing substituents ($-CONH_2$, $-COOCH_3$, and $-COC_6H_5$) yield the corresponding $(NH_3)_5Ru^{II}$ complexes. Reactions with Ti^{III} are kinetically straightforward, exhibit only slight responses to structural alteration, and give no indication of inner-sphere mediation involving the carbonyl group. Kinetic profiles for In(I) reductions of the 3-$CONH_2$, 3-$COOCH_3$, and 3-COC_6H_5-substituted complexes (in the range $[H^+] = 0.030-0.15$ M) begin with a nearly linear section, with rates independent of [In^{I}], but show curvature during the later stages of reaction. These profiles are consistent with a reaction sequence in which the predominant carbonyl form of the oxidant is hydrated to a more reactive *gem*-diol form ($>C{=}O + H_2O \rightleftharpoons >C(OH)_2$), which undergoes reduction by In^{I}, yielding the observed Ru^{II} product and In^{II}. The latter is then rapidly consumed by a second unit of Ru^{III}. Rate constants for the hydration step giving optimal fit to the experimental curves are 6×10^{-4} s^{-1} (for the 3-$CONH_2$ complex) and 1.3×10^{-3} s^{-1} (for the 3-$COOCH_3$ oxidant). Lower limits for the rate of attack by In^{I} on the active forms of the oxidants are estimated as $10^{3.3}-10^{4.6}$ M^{-1} s^{-1}, about 10^2-10^3 times are rapid as the reduction of the unsubstituted pyridine complex. Our results suggest the utilization, by In^{I}, of a hydroxyl-bridged path featuring the sequence In$^{I}-$OH$-$C(OH)$-$py in these reductions, a path which is overshadowed, in the case Ti^{III} reactions, by a more facile outer-sphere process.

The reactions of metal-center oxidants featuring carbonyl-containing organic ligands have played a sizable role in our understanding of the details of intermolecular electron transfer processes in solution. Carboxylato derivatives of $(NH_3)_5Co^{III}$ were the original oxidants used to establish redox mediation by an organic unit.[2] Attack on such complexes by substitution-labile reductants (of which Cr^{2+}(aq) was the prototype) was presumed, and eventually demonstrated,[3] to occur at the carbonyl oxygen, $-C(=\mathit{O})-OCo^{III}$. In addition, incorporation of carbonyl-bearing functions (e.g., aldehyde, keto, ester, or carboxamide fragments) at more remote but properly positioned sites may induce dramatic enhancements in rates of reduction by Cr^{2+}, Eu^{2+}, and U^{3+},[4] attributable, in many instances, to preliminary 1e reduction of the ligand by these strongly reducing ($E°$ -0.40 to -0.63 V) cations.[5]

When a pendant carbonyl group is substantially converted, by hydration, to a *gem*-diol function ($>C{=}O + H_2O \rightleftharpoons >C(OH)_2$), interconversion bewteen the two forms may be reflected in kinetic patterns for reduction. Thus, the $(NH_3)_5Co^{III}$ derivative of glyoxylic acid, ($O{=}CHCOOH$), which exists in solution predominantly as the hydrated cation, **I**, is reduced by Cr^{2+} at a rate determined mainly by its dehydration (1).[6a] However, the more weakly reducing center, $Ti(OH)^{2+}$, utilizes the diol form, **I**, preferentially and is found to reduce this oxidant more rapidly than a number of carbonyl-substituted complexes which are negligibly hydrated in solution.[7]

$$\underset{\textbf{I}}{(OH)_2CHCOOCo^{III}} \rightleftharpoons \underset{\textbf{II}}{O{=}CHCOOCo^{III}} + H_2O \qquad (1)$$

This study deals principally with reductions by In^+, a hypovalent s-electron donor, of oxidants featuring a carbonyl function. Since a number of Co(III)−In(I) reactions of this type have been found to be inconveniently slow,[8] we have chosen Ru(III)-derived acceptors. Related reductions by Ti(III) are included for comparison.

Experimental Section

Materials. Indium(I) solutions were prepared and handled under argon using a modification[8] of the procedure of Headridge,[9] and their In(I) content was estimated iodimetrically as described.[8] Titanium(III) solutions were prepared, stored, and standardized as described by Ram.[7]

The ruthenium(III) complexes $[NH_3)_5Ru^{III}(Lig)]^{3+}(ClO_4^-)_3$ were prepared from $Cl(NH_3)_5Ru^{III}Cl_2$ by slight modifications[10] of the procedure of Gaunder.[11] Ultraviolet spectra of these complexes corresponded closely to those described.[11] Elemental analyses (C, H, N) of the complexes of 3-benzoylpyridine ($\epsilon_{262}^{\max}$ 15.6×10^3) and 4-benzoylpyridine ($\epsilon_{271}^{\max}$ 13.6×10^3 M^{-1} cm^{-1}) were in accord with the assigned structures. Strong C═O stretching peaks (KBr pellet) were observed for the solid 3-$CONH_2$py (1665 cm^{-1}), the 3-$COOCH_3$py (1728 cm^{-1}), and the 3-C_6H_5COpy (1658 cm^{-1}) complexes.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon in solutions which were 0.03 M in $HClO_4$ and 0.20 M in $NaClO_4$. Reactions were monitored near the low-energy maximum of the Ru(II) product (the MLCT band near 470 nm). Measured deficient quantities of the reductant were added to a known excess of

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(2) Taube, H. *J. Am. Chem. Soc.* **1955**, *77*, 4481.

(3) Scott, K. L.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1832.

(4) (a) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639. (b) Gould, E. S.; Johnson, N. A.; Morland, R. B. *Inorg. Chem.* **1976**, *15*, 1929. (c) Goli, U. B.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 221.

(5) Gould, E. S. *Acc. Chem. Res.* **1985**, *18*, 22.

(6) (a) Price, H. J.; Taube, H. *J. Am. Chem. Soc.* **1967**, *89*, 269. (b) For a closely related study, see: Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457.

(7) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103.

(8) Chandra, S. K.; Gould, E. S. *Inorg. Chem.* **1996**, *35*, 3881.

(9) Headridge, J. S.; Pletcher, D. *Inorg. Nucl. Chem. Lett.* **1967**, *5*, 475.

(10) Chandra, S. K.; Gould, E. S. *Inorg. Chem.* **1997**, *36*, 3485.

(11) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627. Because of the explosive character of organic ruthenium perchlorates, *all work with these complexes was carried out on quantities of 200 mg or less.*

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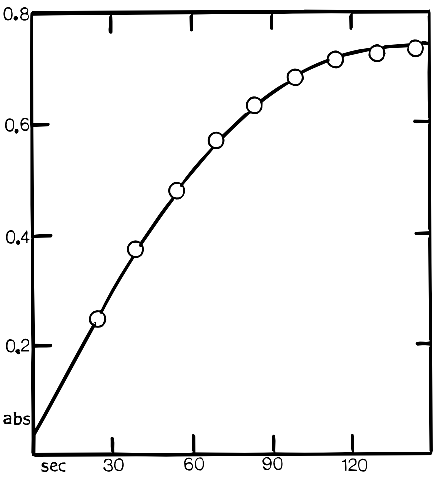


Figure 1. Kinetic profile at 460 nm for the reduction of the 3-carbomethoxypyridine derivative of $(NH_3)_5Ru^{III}$ (**III**, R = 3-COOCH$_3$) (1.80 mM) with In^+_{aq} (0.079 mM) in 0.150 M $HClO_4$ at 25 °C; μ = 0.20 M ($NaClO_4$). The circles are experimental values, whereas the solid line represents absorbances calculated from numerical integration of differential equations based on sequence (4)−(5) in the text with k_4 taken as 3.5×10^{-3} s^{-1} and the ratio k_{-4}/k_5 taken as 7.4×10^{-5} M. The extinction coefficient used for the Ru(II) product is 4.3×10^3 M^{-1} cm^{-1}, and other species were considered to be negligibly absorbent. Optical path length = 1.00 cm.

the Ru(III) oxidant. After 60 s reaction times, increases in absorbance were compared with values calculated from the molar absorbances of the resulting $[(NH_3)_5Ru^{II}(Lig)]^{2+}$ complexes as determined from measurements of pure samples of the latter. Such measurements yielded stoichiometries $\Delta[Ru^{II}]/\Delta[In^I] = 1.94 \pm 0.05$.

Kinetic Experiments. Reactions, under argon, were examined at or near the high-wavelength maximum of the Ru(II) product, using either a Cary 14 instrument or a Durrum-Gibson stopped-flow spectrophotometer[12] interfaced with an OLIS computer system. Ionic strength was regulated by addition of $NaClO_4/HClO_4$. Reductions with Ti(III) were carried out with the reductant in excess, whereas those with In(I) were run with Ru(III) in excess to avoid formation and precipitation of elementary ruthenium.[10] Concentrations of reagents were generally adjusted so that no more of 10% of the reactant in excess was consumed in the reaction. Reductions by Ti(III) yielded simple exponential curves, and rate constants were obtained by nonlinear least-squares fitting to the relationship describing pseudo-first-order decay. These reactions were first order in both redox partners.

In contrast, curves from reduction by In^I (taken in deficiency) of the 3-carbonyl-substituted Ru^{III} complexes approached linearity during the early stages of reaction, with rates quite insensitive to the concentration of reductant, but exhibited more pronounced curvature during the later stages (see, for example, Figure 1). Linear character was most marked with the 3-benzoylpyridine derivative. Addition of the redox products (the respective Ru^{II} complex or In^{3+}) was without perceptible effect on these curves. Fits of such profiles to a proposed sequence, featuring a preliminary step not involving the reductant, were achieved by comparing observed curves to those generated by numerical integration of differential equations based on the suggested mechanism.

Preliminary examination of the reductions of the analogous 4-carbonyl-substituted oxidants (4-COOMe and 4-COC$_6$H$_5$) indicated that these react between 10 and 100 times as rapidly as the corresponding 3-substituted derivatives, with reactions complicated by strong autocatalysis by the Ru(II) product. Work on these systems is continuing.

Table 1. Reductions of Pentaammineruthenium(III) Complexes, $[(NH_3)_5Ru^{III}(Lig)]^{3+}$, with Titanium(III)[a]

Lig	[H$^+$], M	k, M^{-1} s^{-1}
pyridine	1.0	6.4
		21[b]
		26[c]
4-benzoylpyridine (**III**, R − 4-COC$_6$H$_5$)	1.0	24
	0.50	49
	0.20	116
	0.10	2.3×10^2
nicotinamide (**III**, R = 3-CONH$_2$)	1.0	55
methyl isonicotinate (**III**, R = 4-COOCH$_3$)	1.00	70
3-benzoylpyridine (**III**, R = 3-C$_6$H$_5$CO)	1.0	14.5

[a] Reactions were carried out at 22 °C in ClO_4^- media unless otherwise indicated; μ = 1.0 M; [Ti^{III}] = 6.0−8.8 mM; [Ru^{III}] = 0.065−0.13 mM. [b] Value calculated from the data of Davies.[13] Reactions were run at 25 °C in solutions 0.5 M each in HCl and $HClO_4$. [c] Reaction in 1.0 M HCl (this work).

Results and Discussion

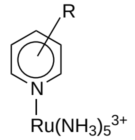
The stoichiometry observed for the reductions by In(I), 1.94 ± 0.05 mol of Ru(III)/mol of In(I), is in accord with formulation of these reactions as (2). Reductions by Ti(III) have earlier been

$$2Ru^{III} + In^{I} \rightarrow 2Ru^{II} + In^{III} \qquad (2)$$

shown to conform to 1:1 stoichiometry (3).[13]

$$Ru^{III} + Ti^{III} \rightarrow Ru^{II} + Ti^{IV} \qquad (3)$$

Rate data for the Ti(III) reductions are summarized in Table 1. The value pertaining to the pyridine-substituted oxidant in 1.0 M HCl (26 M^{-1} s^{-1} at 22 °C) is consistent with that calculated[14] (21 M^{-1} s^{-1} in 0.5 M HCl + 0.5 M $HClO_4$ at 25 °C) from the data of Davies.[13] The observed difference resulting from substitution of Cl^- for ClO_4^- in the supporting electrolyte serves to remind us that rates of electron transfer between charged reactants may be subject to substantial specific medium effects, even at constant ionic strength.[15] The observed kinetic acidity pattern for the 4-benzoylpyridine complex (**III**,R = 4-C$_6$H$_5$CO), a rate very nearly proportional to 1/[H$^+$], is quite usual for reduction by $Ti(III)_{aq}$[13,16] and may be assumed to apply to the remaining oxidants as well. This dependency implicates the deprotonated cation, $Ti(OH)^{2+}$, as the active reducing species. In these cases, specific rates for the latter form may be estimated by dividing the values in 1.0 M H$^+$ by 0.012, the reported[17] K_A value for $Ti(III)_{aq}$ in aqueous ClO_4^-.



III

In the comparison of the Ti(III) rates in 1.0 M $HClO_4$, the most notable feature is the very slight response to structural alteration in the heterocyclic ligand. For the reductions, by Cr^{2+} and Eu^{2+}, of the analogous derivatives of $(NH_3)_5Co^{III}$, attach-

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[12] Kinetic profiles for reductions by In^I were significantly more reproducible when taken on the Cary instrument. We suspect that experiments on the Durrum-Gibson apparatus were complicated by contamination with suspended or dissolved iron arising from rusting of the steel valve parts, but these difficulties persisted even when the flow system was rinsed, before each series of runs, with aqueous $H_2C_2O_4/NaHC_2O_4$ and then with distilled water.

[13] Davies, K. M.; Earley, J. E. *Inorg. Chem.* **1978**, *17*, 3350.

[14] Inverse proportionality between rate and [H$^+$] was demonstrated[13] for this and related systems.

[15] See, for example: Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545. We have shown, however, that addition of 0.03 M Cl^-, the concentration assoiated with the added Ti(III), is without perceptible effect in the reactions at hand.

[16] (a) Earley, J. E.; Bose, R. N.; Berrie, B. H. *Inorg. Chem.* **1983**, *22*, 1836. (b) Thompson, G. A. K.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 638. (c) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1973**, *14*, 873.

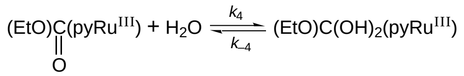
[17] Birk, J. P. *Inorg. Chem.* **1975**, *12*, 580.

ment of the 4-benzoyl group to the pyridine ring results in 10^5–10^7-fold accelerations,[4ab] whereas the same substitution in the Ru(III)–Ti(III) series is seen to be reflected in a much more modest 4-fold enhancement. The latter increase is comparable to that observed[4a] when the corresponding Co(III) oxidants are reduced by the outer-sphere reductant $Ru(NH_3)_6^{2+}$. The implication here is then that the very rapid carbonyl-mediated path dominating the Co(III)–Cr(II) and Co(III)–Eu(II) reactions is not operative in these Ru(III)–Ti(III) systems, which utilize only an outer-sphere route. This conclusion, which presumably extends to the less-effectively bridging $-COOCH_3$ and $-CONH_2$ units, is in accord with that expressed by Davies.[13]

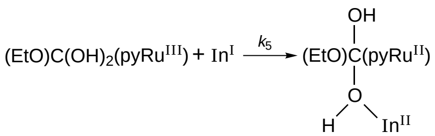
Kinetic traces for the In(I) reductions of the 3-$CONH_2$, 3-$COOCH_3$-, and 3-COC_6H_5-substituted oxidants, taken with Ru(III) in excess, begin with a *nearly linear section* during which rates are only marginally dependent on the concentration of the reductant (e.g., Figure 1). Two quite different interpretations of such profiles come to mind. In the first, the conversion is catalyzed by a reaction product, with the consumption of the reactants being compensated (in full, or in part) by the growth of catalyst. This possibility is ruled out by the inability of either of our products (Ru^{II} and In^{3+}) to catalyze the principal transformation.

The alternative, a sequence in which the initial step does not involve the reductant, brings to mind Price and Taube's description[6] of the Cr^{2+} reduction of the glyoxalato derivative of $(NH_3)_5Co^{III}$ (**I** ⇔ **II**). At low acidities in water, the reduction rates of Price's oxidant were determined principally by the dehydration of the predominant, but relatively inactive, *gem*-diol form (**I**) of this complex to its much more reactive keto form (**II**). There is, however, an important difference. The Ru(III) oxidants in this study have been shown, by both their infrared spectra and their ^{13}C NMR spectra, to exist predominantly as C═O forms.

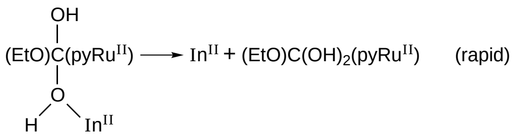
We therefore propose that the initial [In^I]-independent section of each of these mixed-order profiles reflects the slow conversion of the prepoderant form of our carbonyl-substituted oxidant to a $C(OH)_2$ species, which, as is the case with $Ti(OH)^{2+}$–Co(III) systems,[7] is much more reactive than the C═O form, and that the redox act involving In^I becomes kinetically significant when In^I is nearly exhausted. The suggested sequence may then be represented by (4)–(7). The redox step (5) may be further subdivided into the formation of a Ru^{III}–In^I precursor complex and internal electron transfer within that complex, but these steps are, at this point, kinetically inseparable. A similar division may apply also to the Ru^{III}–In^{II} redox (7), which on the basis of previous electron transfer studies[8,10] involving indium, may be taken to be much faster than the reduction by In(I). Dissociation of the Ru^{II}–In^{II} "successor complex" (6) is likewise assumed to be very rapid and, hence, kinetically silent.



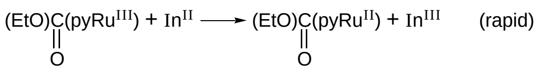
$$\mathrm{(EtO)}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{(pyRu^{III})} + \mathrm{H_2O} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{(EtO)C(OH)_2(pyRu^{III})} \qquad (4)$$



$$\mathrm{(EtO)C(OH)_2(pyRu^{III})} + \mathrm{In^{I}} \xrightarrow{k_5} \mathrm{(EtO)}\underset{\underset{\mathrm{H}\diagup\ \diagdown\mathrm{In^{II}}}{\overset{|}{\mathrm{O}}}}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{(pyRu^{II})} \qquad (5)$$



$$\mathrm{(EtO)}\underset{\underset{\mathrm{H}\diagup\ \diagdown\mathrm{In^{II}}}{\overset{|}{\mathrm{O}}}}{\overset{\overset{\mathrm{OH}}{|}}{\mathrm{C}}}\mathrm{(pyRu^{II})} \longrightarrow \mathrm{In^{II}} + \mathrm{(EtO)C(OH)_2(pyRu^{II})} \quad \text{(rapid)} \qquad (6)$$



$$\mathrm{(EtO)}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{(pyRu^{III})} + \mathrm{In^{II}} \longrightarrow \mathrm{(EtO)}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{(pyRu^{II})} + \mathrm{In^{III}} \quad \text{(rapid)} \qquad (7)$$

Table 2. Representative Kinetic Data for Reductions, Using In^I(aq), of 3-Substituted Pyridine Derivatives of $(NH_3)_5Ru^{III}$ (III)[a]

oxidant	λ, nm	[Ru^{III}], mM	[In^I], mM	[H^+], M	$10^{-4}k_4$,[b] s^{-1}	$10^{-5}k_{-4}/k_5$,[b] M
III, R = 3-$CONH_2$	460	3.4	0.100	0.060	6.2	2.3
		3.3	0.088	0.120	6.0	4.0
		3.0	0.086	0.150	5.2	2.1
III, R = 3-$COOCH_3$	460	0.72	0.092	0.030	11	2.2
		1.00	0.096	0.060	16	2.8
		1.00	0.082	0.090	13	2.6
		1.10	0.081	0.120	12	1.9
		1.80	0.087	0.150	12	1.9
III, R = 3-COC_6H_5	480	0.59	0.089	0.030	48	1.2
		0.59	0.095	0.060	36	0.93
		0.59	0.097	0.090	26	0.65
		0.59	0.095	0.120	22	0.55
		0.59	0.085	0.150	19	0.50

[a] Reactions were carried out under argon at 24 ± 1 °C and ionic strength 0.20 M ($HClO_4$–$NaClO_4$). [b] Parameters were obtained from the best fit to integrated forms of sequence (4)–(5) in the text. "Follow-up" reactions (6) and (7) were assumed to be rapid and kinetically silent.

Expression of this sequence as a series of differential equations and numerical integration using an adaptation of the program KINSIM[18] yielded the concentrations of the participating species at appropriate time intervals during the course of each reaction, and incorporation of the extinction coefficient of the Ru(II) product (the only absorbing species at the wavelength chosen) yielded calculated values for the absorbance of the reaction mixture at each point.

Rate parameters giving optimal agreement between calculated and observed values for all three Ru(III) oxidants are listed in Table 2.[19] Note that the rate constants in the proposed sequence are not wholly independent. Experiments in the range examined allow us to estimate the quotient k_{-4}/k_5 but not the two individual values. Absorbances calculated from the parameters in Table 2 are compared to a representative experimental curve in Figure 1.

As mentioned in connection with earlier treatments of this sort,[20] the resulting parameters must be considered less precise than those pertaining to systems requiring just one rate constant per run. Values for the ratio k_{-4}/k_5, which are obtained mainly from the final stages of each transformation, exhibit particularly severe scatter. Nevertheless, it is clear that both parameters for the 3-benzoyl oxidant decrease steadily with [H^+], whereas those for the 3-$CONH_2$ and 3-$COOCH_3$ complexes follow no clear-cut acidity dependence.

Values of k_4, associated with the hydration of the keto form (**IV**) of the benzoyl derivative to its redox-active *gem*-diol form (**V**), conform to (8),which describes partial conversion of **IV**

$$k_4 = \frac{k_A K_{HA}}{[H^+] + K_{HA}} \qquad (8)$$

to its conjugate acid (**IV′**), which appears to be negligibly active

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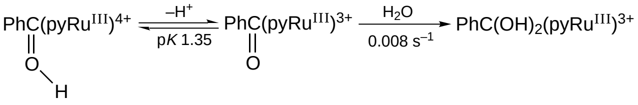
(18) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. We thank Dr. carl Frieden for the original KINSIM program, which was developed for use on a VAX computer system. This was modified, using FORTRAN-77, to a "fixed-length" format and executed on an IBM 3081D system.

(19) "Trial values" for k_4 were chosen from the slope of each curve very shortly after mixing. Estimated values for the ratio k_{-4}/k_5 were obtained from the final stage of each profile where the overall rate constant approaches the quotient k_4k_5/k_{-4}.

(20) (a) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349. (b) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 899.

in the hydration process. Refinement of the acidity data pertaining to k_1 for this complex yields a pK_A value of 1.35 ± 005 and a "limiting" rate constant (k_A) of (8.1 ± 0.6) × 10^{-3} s^{-1} for hydration to diol **V**.



$$\underset{\mathbf{IV'}}{PhC(=OH)(pyRu^{III})^{4+}} \xrightleftharpoons[pK\ 1.35]{-H^+} \underset{\mathbf{IV}}{PhC(=O)(pyRu^{III})^{3+}} \xrightarrow[0.008\ s^{-1}]{H_2O} \underset{\mathbf{V}}{PhC(OH)_2(pyRu^{III})^{3+}}$$

IV′ **IV** **V**

Note that the quotient k_4k_5/k_{-4} remains very nearly constant for each set of experiments with a given oxidant. Since k_4/k_{-4} ($=K_4$) should not vary with acidity, k_5 (pertaining to the electron transfer step) must likewise be acid-independent. If it is assumed further that less than 1% of the oxidant exists, in equilibrium, as the $C(OH)_2$-substituted species (i.e., if $K_4 < 0.01$), we may estimate lower limits for k_5 as 2 × 10^3 M^{-1} s^{-1} (3-$CONH_2$), 6 × 10^3 (3-$COOCH_3$), and 4 × 10^4 (3-COC_6H_5), values which exceed the rate constant for In^I reduction of the unsubstituted pyridine complex (6 M^{-1} s^{-1})[10] by 2−3 powers of 10.

The magnitude of these limits suggests the operation of an additional mechanistic path. The ligands chosen here are known to mediate some reactions in the $Co^{III}-Cr^{II}$ and $Co^{III}-Eu^{II}$ redox series by the radical ion mechanism, in which a 1e reduction of the ligand precedes internal electron transfer to the Co^{III} canter.[5] In such cases, however, initial attack involves the C=O form of the ligand rather than the hydrated $-C(OH)_2$ species. We believe it likely therefore that In^I, which appears to operate through the *gem*-diol form, utilizes an In^I-OH-C linkage in a manner analogous to that demonstrated for $Ti(OH)^{2+}$ in reductions of a number of hydroxylated Co(III) complexes.[7] Our experiments, however, give no hint as to how the migrating electron then reaches the N-bound Ru(III) center to consummate the redox process.

It is perhaps unexpected that In^I chooses a hydroxyl-bridged path formerly suggested for reductions by $Ti(OH)^{2+}$,[7] whereas the latter cation reacts, without appreciable redox bridging, with the Ru(III) oxidants at hand. We suspect that, with Ti(III)−Ru(III) systems, any inner-sphere contribution is overshadowed by a prominent outer-sphere component, a reflection of the much greater self-exchange rate associated with the d center: $(TiOH)^{3+/2+}$, >3 × 10^{-4} M^{-1} s^{-1};[21] $In^{2+/+}$, 10^{-9} M^{-1} s^{-1}.[10]

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(21) Brunschwig, B. S.; Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731.