Electron Transfer. 147. Reductions with Gallium(I)[1]

Shawn Swavey,* V. Manivannan, and Edwin S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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Solutions 0.03−0.05 M in gallium(I) can be generated by treatment of the "mixed" halide $Ga^IGa^{III}Cl_4$ with cold water under argon and then removing the precipitated metallic gallium and $Ga(OH)_3$ by centrifugation. Ga(I) is lost from such preparations with a half-life of about 3 h at 0 °C. These solutions, which may be handled by conventional techniques, readily reduce I_3^-, $IrCl_6^{2-}$, $Fe(bipy)_3^{3+}$, $Fe(NCS)^{2+}$, aquacob(III)alamin, and a group of ring-substituted derivatives of $Ru(NH_3)_5(py)^{3+}$ but are inert to $(NH_3)_5CoCl^{2+}$ and $(NH_3)_5CoBr^{2+}$. All reactions give Ga(III). Reduction of $HCrO_4^-$ in 2-ethyl-2-hydroxybutanoate buffers (pH 3.6) yields a Cr(IV) chelate of the buffering anion but forms Cr(III) when carried out in 0.01 M H^+. Reactions of 1e$^-$ oxidants proceed via successive single changes with the conversion Ga(II) → Ga(III) much more rapid than Ga(I) → Ga(II). Only for the reactions of I_3^- and $Fe(NCS)^{2+}$ is there evidence for redox bridging.

Accounts dealing with the generation of gallium(I) derivatives in aqueous media are unusually scarce,[2,3] and we have not yet encountered descriptions of redox studies of this atypical state. A standard potential for Ga(III,I), −0.755 V (25 °C), has been documented,[2] but supporting data are elusive. In accord with our interest in reductions by main group reducing species,[4] we have chosen, in our pursuit of Ga(I)$_{aq}$, the crystalline "dichloride" (Ga_2Cl_4) as a source of hypovalent gallium. This halide is known to feature equal numbers of Ga(I) and Ga(III) centers ($Ga^IGa^{III}Cl_4^-$).[5]

We here report the preparation of gallium(I) solutions which can be handled using conventional techniques. These have allowed us to compare the reactivities of this s^2 center with a variety of oxidants. A preliminary communication[6] describes a portion of these results.

Experimental Section

Materials. Solutions were prepared using Millipore water that had been boiled for 2 h and then sparged with N_2 for 2 h more to remove dissolved O_2. Sodium perchlorate (used as a supporting electrolyte) was prepared in solution from $NaHCO_3$ and concentrated $HClO_4$. Potassium dichromate, 2-ethyl-2-hydroxybutanoic acid, anhydrous gallium dichloride (Ga_2Cl_4, 99.999%), trifluoromethanesulfonic acid (triflic acid) (Aldrich products), KI_3 solution, potassium iodide (Fisher), iron(III) perchlorate (Alfa), hydroxocobalamin (B_{12a}) hydrochloride (Sigma), and sodium thiocyanate (Mallinckrodt) were used as received. Fresh solutions of sodium hexachloroiridate(IV) (Na_2IrCl_6, $\epsilon_{489}^{max} = 4.1 \times 10^3$ M^{-1} cm^{-1})[7] (Aldrich) were prepared just before use. Stock solutions of $Fe(bipy)_3(PF_6)_3$ (Aldrich) were prepared in dry acetonitrile and were filtered before use. Bromopentaamminecobalt(III) perchlorate ($[Br(NH_3)_5Co]^{2+}[ClO_4^-]_2$) and its chloro analogue were prepared as described.[8]

Substituted pyridinepentaammineruthenium(III) complexes were prepared as their trifluoromethanesulfonte (triflate) salts rather than as the dangerously explosive perchlorates. In a modification of the method of Gaunder,[9] 200 mg (0.69 mmol) of $[ClRu(NH_3)_5]Cl_2$ (Alfa) and 352 mg (1.37 mmol) of CF_3SO_3Ag (Aldrich) were dissolved in 4.0 mL of water and digested hot, and the precipitated AgCl was removed by filtration. A 2-fold excess of the heterocyclic ligand and an excess of zinc amalgam were added to the filtrate, and stirring was continued for 15 min, yielding the intensely colored Ru(II) complex $[(Lig)Ru-(NH_3)_5]^{2+}$; the progress of this conversion was monitored spectrophotometrically. The unreacted amalgam was filtered off, and 300−600 mg of CF_3SO_3Ag was added with stirring. After 2−3 min, the precipitated Ag metal was removed, 0.30 mL of triflic acid was added, and the mixture was cooled for 30−60 min. The crystalline product was filtered off and washed with anhydrous ether, ice-cold ethanol, and again with ether. The faintly colored Ru(III) triflates were stored in a desiccator and protected from light. Yields were 40−80%. Elemental analyses (C, H, N) of these complexes (Atlantic Microlabs) were consistent with the assigned structures.

Gallium(I) solutions were prepared by dissolving 1.0−1.5 g of Ga_2Cl_4 in 6−8 mL of distilled water in an ice bath under a constant flow of protective N_2 or argon. Metallic gallium immediately precipitates, and the solution evolves H_2. The preparation was centrifuged, yielding a pale-yellow solution and a metallic solid. The supernatant was found to be 0.05 M in Ga(I) (spectrophotometric titration vs KI_3 at 353 nm).[10] Upon standing, Ga(I) gradually decreases. After 3 h at 0 °C, only half

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(10) This preparation gives yields of Ga(I) about one-fourth those resulting from a previous procedure[6] in which Ga_2Cl_4 was first dissolved in acetonitrile and the resulting solution was then diluted with water. However, the aqueous solutions obtained are free from acetonitrile, which in some cases appears to affect kinetic behavior slightly. Only 10−20% of the Ga(I) in the starting material is obtained in solution. The precipitated material is a mixture of gallium metal, obtained from disproportionation of Ga(I), and $Ga(OH)_3$. These solutions sometimes become cloudy on standing probably because of the precipitation of traces of $Ga(OH)_3$. When this occurred, the preparation was centrifuged again, and the supernatant, after reanalysis for Ga(I), was used in further experiments.

Table 1. Stoichiometry of Redox Reactions of Ga(I)[a]

Ox	$E°$,[d] V	[H$^+$], M	λ, nm	Δ[Ox]/Δ[Ga(I)]
I$_3^-$	0.54	0.020	352	1.02 ± 0.03
[Ir^{IV}Cl$_6$]$^{2-}$	0.89	0.020	488	1.95 ± 0.06
aquacob(III)alamin (B$_{12a}$)	0.30	0.020	530	b
HCrO$_4^-$ (unbuffered)	0.49^e	0.010	350	0.65 ± 0.01
HCrO$_4^-$,^{c} (EHB$^-$)		c	511	1.08 ± 0.09
[Fe^{III}(bipy)$_3$]$^{3+}$	0.97	0.020	520	1.91 ± 0.06
[Fe^{III}(NCS)]$^{2+}$	0.70	0.020	462	2.00 ± 0.10
[(pyridine)(NH$_3$)$_5$Ru]$^{3+}$	0.31	0.020	408	b
[(4-acetylpyridine)(NH$_3$)$_5$Ru]$^{3+}$	~0.5	0.020	520	2.01 ± 0.08
[(3-acetylpyridine)(NH$_3$)$_5$Ru]$^{3+}$	~0.4	0.020	413	1.96 ± 0.04
[(4-carbomethoxypyridine)(NH$_3$)$_5$Ru]$^{3+}$	0.39	0.020	497	2.05 ± 0.06

[a] Reactions were carried out at 23 °C. Waiting periods were 2.0−15.0 min. Ox = oxidant. [b] Very slow reactions; decompositions competed with the redox of interest. [c] Cr(VI) was added as K$_2$Cr$_2$O$_7$. Solutions were buffered with equal concentrations (0.05 M each) of the ligand 2-ethyl-2-hydroxybutanoic acid (EHBA) and its sodium salt (Na$^+$EHB$^-$). [d] Potentials mainly from ref 17. [e] $E°$ for Cr(VI,III) adjusted to pH 2.

of the reductant remains, and about 5% survives after 48 h. Reproducible kinetic experiments most often utilized reductant solutions 2.5−4 h after their preparation,[11] and even within this period, capricious behavior was occasionally encountered. For slow reactions (e.g., reductions of B$_{12a}$) analyses for Ga(I) should be carried out just before and just after each run.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon and monitored at or near the low-energy maximum of each oxidant. Measured deficient quantities of Ga(I) were added to a known excess of the oxidant. After 2−15 min waiting periods, decreases in absorbance were compared to the initial known absorbance of the oxidant. Results are summarized in Table 1.

Kinetic Studies. Reactions, under argon, were generally examined at or near λ_{max} of the oxidant, using either a Shimadzu-1601 instrument or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 23.0 ± 0.5 °C throughout the entire series of experiments. Ionic strength was regulated by addition of NaClO$_4$/HClO$_4$, NaCl/HCl, or KI. To minimize loss of Ga(I) in acidic media, reactions were initiated by mixing Ga(I) solutions in 0.5 M NaClO$_4$ with oxidant solutions of appropriate acidity. Quantities of reagents were most often chosen so that no more than 10% of that reactant in excess was consumed by the redox transformation. Stopped-flow runs with Ga(I) in excess were repeated until three successive kinetic curves were superimposible, and a group of runs with a given oxidant was repeated until a reproducible kinetic pattern was established. All reactions were first order in Ga(I).[12] Rate constants were evaluated by nonlinear least-squares fitting to the relationship describing first-order decay.
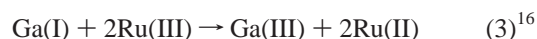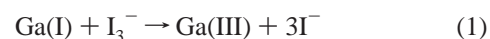
Additional Observations. Under our conditions, Ga(I) is unreactive toward both (NH$_3$)$_5$CoCl^{2+} and (NH$_3$)$_5$CoBr^{2+}. Reaction with aquacobalamin (B$_{12a}$) in 0.01 M H$^+$ yields cob(II)alamin (B$_{12r}$).[13] There is no distortion of the decay curve attributable to the formation or the consumption of cob(I)alamin (B$_{12s}$). Reduction of HCrO$_4^-$ in 2-ethyl-2-hydroxybutanoate buffer (HEBA/EBA$^-$) yielded the Cr(IV) derivative of this carboxylato chelate, as indicated by its spectrum (λ_{max} 510 nm),[15] but the kinetic profiles associated with this conversion could not be meaningfully interpreted.

Reactions of the Ru(III) complexes of 4-substituted pyridines yielded dark-red solutions exhibiting metal-to-ligand charge-transfer spectra characteristic of the corresponding ruthenium(II) derivatives.[9,16]
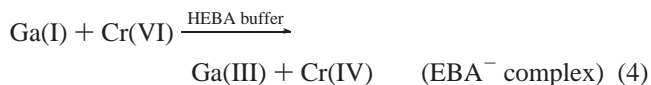
Results and Discussion

The most notable observation in the present study is probably the negligible redox reactivity of our reductant solutions toward (NH$_3$)$_5$CoCl^{2+} and its Co(III)Br analogue. These Co(III) oxidants offer remarkably facile inner-sphere le$^-$ paths to aqua complexes of d- and f-block donors,[17] but such halogen-mediated routes are effectively denied to the isoelectronic 4s^2 pair Ge(II)^{4d} and Ga(I). The homologous center In(I), also principally a 2e$^-$ reagent, reacts, somewhat reluctantly and in single electron steps, via such paths,[4b] but the smaller s^2 cations respond mainly to those le$^-$ oxidants featuring strongly positive potentials and high le$^-$ self-exchange rates.

Results of stoichiometric experiments, summarized in Table 1, indicate that Ga(I) reacts with an equimolar quantity of I$_3^-$ but consumes very nearly 2 equiv of the various le$^-$ oxidants. In each case the product is, as expected, Ga(III).

$$Ga(I) + I_3^- \rightarrow Ga(III) + 3I^- \qquad (1)$$

$$Ga(I) + 2IrCl_6^{2-} \rightarrow Ga(III) + 2IrCl_6^{3-} \qquad (2)$$

$$Ga(I) + 2Ru(III) \rightarrow Ga(III) + 2Ru(II) \qquad (3)^{16}$$

Kinetic curves for these transformations generally featured no discontinuities resulting from the buildup or loss of an intermediate on a time scale commensurate to that of the principal conversion. Reduction of HCrO$_4^-$ in solutions buffered by 2-ethyl-2-hydroxybutanoic acid and its anion yields the Cr(IV) chelate of the buffering anion,[15] but reaction at pH 2 in the absence of this carboxylato system gives Cr(III):

$$Ga(I) + Cr(VI) \xrightarrow{\text{HEBA buffer}}$$
$$Ga(III) + Cr(IV) \qquad (EBA^- \text{ complex}) \quad (4)$$

$$3Ga(I) + 2Cr(VI) \xrightarrow{\text{pH 2}} 3Ga(III) + 2Cr(III) \qquad (5)$$

Among the oxidants yielding acceptable kinetic data, only Fe(NCS)$^{2+}$ and aquacobalamin (B$_{12a}$) exhibit appreciable kinetic medium effects. Oxidations by Fe(NCS)$^{2+}$ (Table 2) are retarded

(11) A procedure analogous to that used for In(I)^{4b} (oxidation of In−Hg with silver triflate in acetonitrile) is effectively ruled out by the very limited solubility of elemental gallium in mercury. Spicer, W. H.; Bartholomay, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 868.

(12) When dilute Ga(I) solutions were introduced into our flow system, some loss of reductant resulted from reaction with traces of absorbed O$_2$. Since such losses were proportionately greatest at the lowest concentration, kinetic curves suggested a greater-than-unity order in reductant. This effect disappeared as experiments were repeated.

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Table 2. Kinetic Data for the Reduction of $[Fe^{III}(NCS)]^{2+}$ with Gallium(I)[a]

10^4 [Fe(III))], M	[H$^+$], M	10^3[NCS$^-$], M	$k,$[b] s^{-1}
0.60	0.40	6.0	1.62 ± 0.02 (1.82)
1.20	0.40	6.0	1.67 ± 0.01 (1.82)
1.80	0.40	6.0	1.74 ± 0.02 (1.82)
2.40	0.40	6.0	1.62 ± 0.02 (1.82)
1.80	0.50	6.0	1.34 ± 0.02 (1.77)
1.80	0.30	6.0	1.88 ± 0.02 (1.90)
1.80	0.10	6.0	2.76 ± 0.02 (2.54)
1.80	0.050	6.0	4.0 ± 0.1 (3.5)
1.80	0.010	6.0	11.0 ± 0.6 (11.1)
1.80	0.30	4.0	2.12 ± 0.08 (1.90)
1.80	0.30	3.0	2.22 ± 0.04 (1.90)
1.80	0.30	2.0	2.23 ± 0.04 (1.90)
1.80	0.30	1.0	2.20 ± 0.09 (1.90)

[a] Reactions were carried out at 23 °C; $\mu = 0.50$ M (NaClO$_4$/HClO$_4$); $\lambda = 470$ nm; mixing time 4.5 ms; optical path length 2.0 cm; [Ga(I)] $= 2 \times 10^{-5}$ M throughout. Decomposition of $[Fe^{III}(NCS^-)]^{2+}$ was minimized by addition of 6×10^{-3} M NaSCN. [b] Pseudo-first-order rate constants; parenthetical values were calculated from rate law and parameters in Table 4.

Table 3. Kinetic Data for Reduction of Aquacobalamin (B$_{12A}$) with Gallium(I)[a]

10^4 [Ga(I)], M	[H$^+$], M	[Cl$^-$], M	$10^2 k,$[b] s^{-1}
5.0	0.020	1.00	2.65 ± 0.05 (2.62)
7.0	0.020	1.00	3.5 ± 0.10 (3.7)
10.0	0.020	1.00	5.2 ± 0.2 (5.2)
15.0	0.020	1.00	8.9 ± 0.1 (7.9)
20.0	0.020	1.00	11.6 ± 0.3 (10.5)
25.0	0.020	1.00	13.7 ± 2.2 (13.1)
15.0	0.020	0.10	1.22 ± 0.31 (1.09)
15.0	0.020	0.50	2.15 ± 0.02 (2.73)
15.0	0.020	0.80	5.9 ± 0.1 (5.4)
7.0	0.10	1.00	3.6 ± 0.1 (3.9)
7.0	0.30	1.00	3.2 ± 0.1 (3.9)
7.0	0.50	1.00	3.8 ± 0.2 (3.9)

[a] Reactions were carried out at 23 °C; $\mu = 1.0$ M (NaCl/HCl); $\lambda = 430$ nm; optical path length 1.0 cm; [B$_{12a}$] $= 1.50 \times 10^{-5}$ M. [b] Pseudo-first-order rate constants; parenthetical values were calculated from rate law and parameters in Table 4.

by increases in [H$^+$], whereas the reductions of aquacobalamin (Table 3) are accelerated markedly by added chloride. Rates with Fe(NCS)$^{2+}$ may be correlated by

$$\text{rate} = [Ga^I][Fe^{III}](k + k_{-1}[H^+]^{-1}) \qquad (6)$$

whereas those with B$_{12a}$ conform to

$$\text{rate} = [Ga^I][B_{12a}](k + k'[Cl^-]^2) \qquad (7)$$

Kinetic parameters resulting from treatment of data according to eqs 6 and 7 are summarized in Table 4. Calculated and observed rates are compared at the right in Tables 2 and 3.
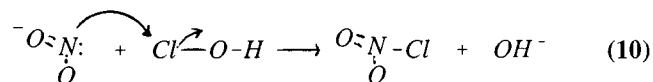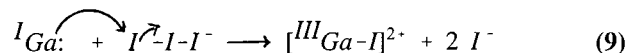
Rate law 6 for the Fe(NCS)$^{2+}$–Ga(I) reaction differs substantially from that reported for the corresponding reduction by In(I).[18] An [NCS$^-$]-proportional term in the latter, attributable to a NCS$^-$-bridged component, has disappeared, and an inverse-[H$^+$] term, almost certainly related to deprotonation of an Fe-(III) center, has become prominent. Within the pH range examined, the preponderant Fe(III) species is [Fe(H$_2$O)$_4$(OH)-(NCS)]$^+$ (rather than Fe(H$_2$O)$_5$(NCS)$^{2+}$; pK_A −0.8).[19] We are then dealing with the preequilibrium

$$[Fe(NCS)(H_2O)_4(OH)]^+ \overset{K_A}{\rightleftharpoons} [Fe(NCS)(H_2O)_4(OH)_2] \qquad (8)$$

The bimolecular rate constant associated with the active dihydroxo complex, obtained by dividing k_{-1} by 10^{-3} (an estimated K_A),[20] falls near 6×10^5 M^{-1} s^{-1}, a value about 10^2 times that for the [H$^+$]-independent rate (7×10^3 M^{-1} s^{-1}). This ratio strongly suggests an inner-sphere path (possibly involving a μ-(OH)$_2$ bridge) for the k_{-1} component,[21] thus far the sole example for Ga(I) systems.

Kinetic patterns for reduction of the Co(III)-bound corrin system in aquacobalamin (B$_{12a}$) by Ga(I) and In(I)[22] are also quite different. We find no counterpart for the near-linear profiles observed with In(I) at high [Cl$^-$], and the curves obtained with Ga(I), all of them very nearly exponential in character, point to striking acceleration by added Cl$^-$. This effect is often, although not invariably, observed in reductions by s^2 centers that pass through a relatively unstable s^1 intermediate such as Ge(III)[4d] or Sn(III).[23] It implies the preliminary attachment of one or more chlorides to the reducing center, presumably converting it to a configuration of higher coordination number that is more nearly like that of the odd-electron intermediate, in this case Ga(II), a similarity that is thought to lower the Franck–Condon barrier to the initial s^2 → s^1 transition. It is likely that similar chloride catalysis will operate in other reductions by Ga(I), although we did not observe it in the more rapid conversions occurring with more strongly oxidizing coreagents.

Rate laws are summarized in Table 4. The reduction of I$_3^-$ ($k = 1.2 \times 10^5$ M^{-1} s^{-1} is remarkably rapid, especially in view of its modest reduction potential ($E° = 0.54$ V). This oxidant, alone among those listed, can undergo 2e$^-$ changes complementary to those of Ga(I). A bridged path (reaction 9), involving halogenonium (I$^+$) transfer, analogous to that for the HOCl–NO$_2^-$ (reaction 10),[24] is thus an attractive possibility here.

$$^IGa: \; + \; ^+I\text{-}I\text{-}I^- \longrightarrow [^{III}Ga\text{-}I]^{2+} \; + \; 2\,I^- \qquad (9)$$

$$^-O\text{-}N: \; + \; Cl\text{-}O\text{-}H \longrightarrow O\text{-}N\text{-}Cl \; + \; OH^- \qquad (10)$$

Oxidations by IrCl$_6^{2-}$ and by the complexes of Fe(III) and Ru(III) must, however, react by successive 1e$^-$ steps. The undistorted monophasic kinetic profiles obtained with each of these are consistent with a sequence such as

$$Ga(I) \overset{Ru(III)}{\longrightarrow} Ga(II) \overset{Ru(III)}{\underset{rapid}{\longrightarrow}} Ga(III) + 2Ru(II) \qquad (11)$$
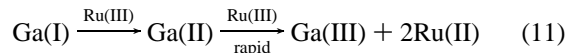
initiated by rate-determining electron loss from Ga(I) preceding a rapid (and kinetically silent) oxidation of a Ga(II) intermediate. As with reductions by In(I)[4b] and Ge(II),[4d] the formation of the odd-electron intermediate is invariably slower than its conversion to the stable s^0 state. This contrast reflects, in part, the much more negative potential of the s^1 species, as has been demonstrated for the Tl(I,II,III)[25] and the In(I,II,III)[26] triads.

The rate enhancements resulting from incorporation of carbonyl-containing (keto or ester) substituents onto pyridine-

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Table 4. Rate Laws and Kinetic Parameters for Oxidations of Gallium(I)[a]

Ox	μ, M	rate law	parameters[b]
I_3^-	0.55 (Cl^-/I^-)	$k[Ga^I][Ox]$	$k = (1.20 \pm 0.06) \times 10^5$
$[Ir^{IV}Cl_6]^{2-}$	0.50 (Cl^-)		$(3.4 \pm 0.2) \times 10^3$
$[Fe^{III}(bipy)_3]^{3+}$	0.20 (ClO_4^-)		$(3.8 \pm 0.3) \times 10^5$
$[(pyridine)(NH_3)_5Ru]^{3+}$	0.10 ($CF_3SO_3^-$)		$(9 \pm 1) \times 10$
$[(4\text{-acetylpyridine})(NH_3)_5Ru]^{3+}$	0.10 ($CF_3SO_3\text{-}$)		$(9.8 \pm 0.2) \times 10^3$
$[(3\text{-acetylpyridine})(NH_3)_5Ru]^{3+}$	0.10 ($CF_3SO_3^-$)		$(5.3 \pm 0.3) \times 10^2$
$[(4\text{-benzoylpyridine})(NH_3)_5Ru]^{3+}$	0.10 ($CF_3SO_3^-$)		$(6.2 \pm 0.2) \times 10^3$
$[(4\text{-carbomethoxypyridine})(NH_3)_5Ru]^{3+}$	0.10 ($CF_3SO_3^-$)		$(7.1 \pm 0.3) \times 10^2$
aquacob(III)alamin (B_{12a})[c]	1.0 (Cl^-)	$[Ga^I][Ox](k + k'[Cl^-]^2)$	$k = 6.8 \pm 0.9$
			$k' = (4.6 \pm 0.2)\ M^{-3}\ s^{-1}$
$[Fe^{III}(NCS)]^{2+\ d}$	0.50 (ClO_4^-)	$[Ga^I][Ox](k + k_{-1}[H^+]^{-1})$	$k = (7.4 \pm 0.7) \times 10^3$
			$k_{-1} = (6.1 \pm 0.8) \times 10^2\ s^{-1}$

[a] Reactions were run at 23 °C; [H$^+$] = 0.01 M unless otherwise indicated. Ox = oxidant. [b] Rate constants in M^{-1} s^{-1} except k' for B$_{12a}$ and k_{-1} for Fe(NCS)$^{2+}$. [c] [H$^+$] = 0.02−0.50 M. [d] [H$^+$] = 0.050−0.50 M.

bound Ru(III) oxidants, although substantial, are much less striking than those recorded for reductions by Cr(II) and Eu(II) (10^4-10^7)[27] when analogous substitutions are carried out on Co(III) oxidants, which serve as prototypes for inner-sphere accelerations in pyridine-ligated systems. It is reasonable then to ascribe such increases in the present instances mainly to withdrawal of electron density by these electron-attracting groups from the acceptor site, a process that is recognized[28] generally to facilitate external electron acceptance. The effect is somewhat more intense with Ru(III) than with Co(III), reflecting the additional participation of pyridine-bound ruthenium in metal-to-ligand π donation. Moreover, the 20-fold rate difference between the 4- and 3-acetyl-substituted oxidants suggests that the intensity of such back-bonding is partially conjugatively dependent, an inference that is bolstered by the much lower λ_{max} observed for the reduction product of the 4-acetyl isomer.[16]

In 1962, Hill and co-workers[29] reported that reductions of B$_{12a}$ by the s^2 center Sn(II) in basic solution yield the Co(I) complex cobalalamin(I) (B$_{12s}$), which was subsequently shown[30]

to react rapidly (at higher acidities) with B$_{12a}$ (Co^I + Co^{III} → 2Co^{II}). It is doubtful, however, that an analogous path is significant for the Ga(I)−B$_{12a}$ reaction in our media. At pH 1−2, the Co(III)-bound hydroxyl is converted virtually completely to the Co(III)−OH$_2$ function, (pK_A near 8.0),[31] which, in contrast to Co(III)−OH, cannot serve effectively as an inner-sphere redox bridge.[32] At the same time, an *outer-sphere* two-unit transfer must be considered to be exceedingly slow (reflecting a prohibitively high Franck−Condon barrier).[17] We suggest therefore that aquacobalamin at low pH oxidizes Ga(I) by a pair of le$^-$ steps analogous to those suggested for the Fe(III) and Ru(III) oxidants here listed.

In summary, our experiments demonstrate that despite occasionally capricious behavior, aqueous solutions of Ga(I) can, with care, be employed in quantitative experiments that require only conventional handling methods.

Moreover, we have begun to see how the balance between 1e- and 2e-reducing character varies among these less usual s^2 centers. Indium(I) reduces a number of Co(III) species that prove to be inert toward both Ge(II) and Ga(I). Single electron action of the last two (4s^2) species requires oxidants of higher potential, preferably in halide-rich media. Thus far, similarities in redox behavior within this trio of donors appear to depend more on outer-shell occupancy than on ionic charge.

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