Aqueous solutions of hypovalent gallium; reductions using gallium(I)†

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Solutions 0.2 mol dm^{-3} in Ga^{I}, prepared by dissolving Ga_2Cl_4 in dry acetonitrile, are stable for more than seven days and may be diluted 300- to 1000-fold with O_2-free water to give Ga^{I} preparations that may be handled by conventional techniques; these Ga^{I}(aq) solutions readily reduce I_3^-, Br_2(aq), $IrCl_6^{2-}$, $Fe(bipy)_3^{3+}$ and aquacob(III)alamin (B_{12a}) but are inert to $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$; reduction of $HCrO_4^-$ in 2-ethyl-2-hydroxybutanoate buffers yields the Cr^{IV} chelate of the buffering anion.

Accounts of the generation of gallium(I) species in aqueous solution are exceedingly scarce,[2,3] and no redox studies of this unusual state appear to have been described. A standard potential for Ga(III,I), −0.755 V (25 °C) has been documented.[2]

The crystalline compound 'gallium dichloride' (Ga_2Cl_4) is known to feature equal numbers of Ga(I) and Ga(III) centers ($Ga^{I}\,Ga^{III}Cl_4^-$).[4] Employing this as a source of hypovalent gallium, we have prepared aqueous Ga(I) solutions which have allowed us, utilizing conventional methods, to compare rates at which this s^2-center reacts with a variety of oxidants.

Manipulations of Ga_2Cl_4 (Aldrich) were carried out under high purity N_2 or Ar. Solutions were prepared by dissolving 1.25 g of this halide in 8.0 ml of anhydrous MeCN under a constant flow of protective gas. After 5 min of stirring, a silver-colored precipitate separates. The clear yellow supernatant solution, which was obtained by centrifuging, was found to be 0.20 mol dm^{-3} in Ga^{I} (spectrophotometric redox titration *vs.* KI_3 at 353 nm) and remained unchanged on standing for seven days. Aqueous solutions for kinetic experiments, prepared by 300- to 1000-fold dilutions of the MeCN solutions with O_2-free water, were stable for 10–15 min in the absence of electrolyte. For slow reactions (*e.g.* reduction of vitamin B_{12a}) fresh aqueous solutions were prepared for each individual run. The rate of the Ga(I)–I_3^- reaction was not appreciably changed by increasing [MeCN] from 0.02 to 0.50 mol dm^{-3}, or by adding $GaCl_3$ in concentration three times that of Ga^{I}.

Solutions of Ga(I) rapidly reduce I_3^-, Br_2(aq), $IrCl_6^{2-}$, $HCrO_4^-$, $Fe(CN)_6^{3-}$ and $Fe(bipy)_3^{3+}$. Reduction of B_{12a} [aquacob(III)alamin] is slow, and there is no perceptible reaction with $Co(NH_3)_5Cl^{2+}$ or $Co(NH_3)_5Br^{2+}$. Each mol of Ga(I) consumes very nearly 1.0 mol of I_3^- or Br_2 but 2.0 mol of the le$^-$ oxidants $IrCl_6^{2-}$ and $Fe(bipy)_3^{3+}$, reflecting the expected conversion to Ga^{III} with oxidants of either type [eqn. (1) and (2)]:

$$Ga^{I} + Br_2 \rightarrow Ga^{III} + 2Br^- \qquad (1)$$

$$Ga^{I} + 2\ Fe(bipy)_3^{3+} \rightarrow Ga^{III} + 2\ Fe(bipy)_3^{2+} \qquad (2)$$

Oxidation by $HCrO_4^-$ utilizes 0.64 ± 0.01 mol of Cr^{VI} in 0.01 M $HClO_4$ but 1.1 mol of oxidant when carried out in 2-ethyl-2-hydroxybutanoic acid buffer (EHBA/EHB$^-$, pH 3.3), indicating predominant conversion to Cr^{III} in the absence of this chelating ligand [eqn. (3)] but formation of Cr^{IV} in its presence [eqn. (4)]:

$$3Ga^{I} + 2\ Cr^{VI} \rightarrow 3\ Ga^{III} + 2\ Cr^{III}\ (\text{pH } 1\text{–}2) \qquad (3)$$

$$Ga^{I} + Cr^{VI} \xrightarrow[\text{buffer}]{\text{EHBA}} Ga^{III} + Cr^{VI}\ (\text{EHB}^-\text{ complex}) \qquad (4)$$

The pink product of eqn. (4) showed a strong peak at 510 nm, typical of EHB-chelated Cr^{IV}.[5]

The reactions listed in Table 1 are first order in each of the redox partners. Although oxidations by $IrCl_6^{2-}$ and $Fe(bipy)_3^{3+}$ almost certainly pass through the intermediate state Ga^{II}, kinetic profiles for these oxidants exhibit no discontinuity attributable to the accumulation or decay of this odd-electron species, implying a two-step sequence (5), in which

$$Ga^{I} \xrightarrow[\text{slow}]{Ir^{IV}} Ga^{II} \xrightarrow[\text{rapid}]{Ir^{IV}} Ga^{III} \qquad (5)$$

the initial step is rate-determining and the more rapid follow-up step is kinetically silent. The relative rates of the two steps suggest that Ga^{II}, the s^1 intermediate, is much more strongly reducing than the parent s^2 cation, a difference applying also to the related p-block triads, Tl(III,II,I),[7] In(III,II,I)[8] and Ge(IV,III,II).[9]

As has been recently noted[1] for Ge^{II} (an isoelectronic state), Ga^{I} resists oxidation by both $Co(NH_3)_5Cl^{2+}$ and by its Co(III)Br counterpart. These Co(III) oxidants offer remarkably facile inner-sphere le$^-$ paths to aqua complexes of d- and f-block reductants,[10] but such routes are denied to this pair of 4s^2 species which react primarily as 2e$^-$ donors. This marked mechanistic shift probably results in part from less effective halo-ligation to this main group center and, in part, from its modestly reducing $E°$(I,II) value (in contrast to the more negative potential for its II–III conversion).

In contrast, we find the cobalt(III) corrin derivative, aquacob(III)alamin (B_{12a}) to be reduced smoothly to its Co(II) analog. We suspect that this reaction is initiated by the two-unit reduction (very likely by oxo-transfer) to the known Co^{I} complex, B_{12s} [cob(I)alamin], a hypovalent species which has been shown[11] to undergo very rapid comproportionation with B_{12a} [eqn. (6)]:

$$Co^{III} \xrightarrow{Ga^{I}} Co^{I} \xrightarrow{Co^{III}} 2\ Co^{II} \qquad (6)$$

Table 1 Reductions with aqueous gallium(I)[a]

Oxidant	Product	k/dm^3 mol^{-1} s^{-1}
I_3^-	I^-	(1.47 ± 0.09) × 10^4
Br_2 (aq)	Br^-	(2.05 ± 0.05) × 10^4
$IrCl_6^{2-}$	$IrCl_6^{3-}$	(7.3 ± 0.05) × 10^2
$Fe(bipy)_3^{3+}$	$Fe(bipy)_3^{2+}$	(8.9 ± 0.2) × 10^4
$HCrO_4^-$ (pH 2.0)	Cr^{III}	(2.7 ± 0.1) × 10^3
B_{12a} (Co^{III})	B_{12r} (Co^{II})[b]	7.1 ± 0.3
$[Co(NH_3)_5Br]^{2+}$		< 0.02
$[Co(NH_3)_5Cl]^{2+}$		< 0.01

[a] Reactions at 25 °C; μ = 0.5 M ($NaClO_4$, LiCl or KI); [H$^+$] = 0.01–0.05 M; [Ga^{I}] = (1.0–12.0) × 10^{-4} M; [oxidant] = (4.0–12.0) × 10^{-5} M. [b] Spectrum of product corresponded to that reported by Pratt.[6]

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† Electron Transfer, part 145. For part 144, see ref. 1.

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