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

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Received (in Cambridge, UK) 19th June 2000, Accepted 25th September 2000
First published as an Advance Article on the web

Solutions 0.2 mol dm^{-3} in Ga^{I}, prepared by dissolving Ga$_2$Cl$_4$ 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$_3$)$_5$Cl^{2+} and Co(NH$_3$)$_5$Br^{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$_2$Cl$_4$) 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$_2$Cl$_4$ (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$_3$)$_5$Cl^{2+} or Co(NH$_3$)$_5$Br^{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)]:

$$\mathrm{Ga^{I} + Br_2 \rightarrow Ga^{III} + 2Br^-} \tag{1}$$

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

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)]:

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

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

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

$$\mathrm{Ga^{I} \xrightarrow[slow]{Ir^{IV}} Ga^{II} \xrightarrow[rapid]{Ir^{IV}} Ga^{III}} \tag{5}$$

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$_3$)$_5$Cl^{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)]:

$$\mathrm{Co^{III} \xrightarrow{Ga^{I}} Co^{I} \xrightarrow{Co^{III}} 2\ Co^{II}} \tag{6}$$

We are grateful to the National Science Foundation for support of this work and to Ms Arla McPherson and Ms Carol Haven for technical assistance.

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$_3$)$_5$Br]$^{2+}$		< 0.02
[Co(NH$_3$)$_5$Cl]$^{2+}$		< 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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