

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 Ga₂Cl₄ in dry acetonitrile, are stable for more than seven days and may be diluted 300- to 1000-fold with O₂-free water to give Ga^I preparations that may be handled by conventional techniques; these Ga^I(aq) solutions readily reduce I₃⁻, Br₂(aq), IrCl₆²⁻, Fe(bipy)₃³⁺ and aquacob(III)alamin (B_{12a}) but are inert to Co(NH₃)₅Cl²⁺ and Co(NH₃)₅Br²⁺; reduction of HCrO₄⁻ in 2-ethyl-2-hydroxybutanoate buffers yields the Cr^{IV} chelate of the buffering anion.

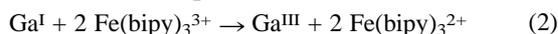
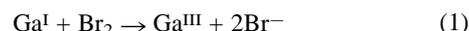
Accounts of the generation of gallium(I) species in aqueous solution are exceedingly scarce,^{2,3} and no redox studies of this unusual state appear to have been described. A standard potential for Ga(III), -0.755 V (25 °C) has been documented.²

The crystalline compound 'gallium dichloride' (Ga₂Cl₄) is known to feature equal numbers of Ga(I) and Ga(III) centers (Ga^IGa^{III}Cl₄).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 s²-center reacts with a variety of oxidants.

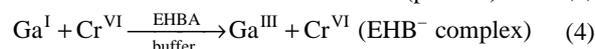
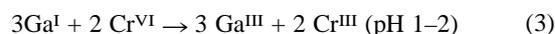
Manipulations of Ga₂Cl₄ (Aldrich) were carried out under high purity N₂ or Ar. Solutions were prepared by dissolving 1.25 g of this halide in 8.0 ml of anhydrous MeCN under a constant flow of protective gas. After 5 min of stirring, a silver-colored precipitate separates. The clear yellow supernatant solution, which was obtained by centrifuging, was found to be 0.20 mol dm⁻³ in Ga^I (spectrophotometric redox titration vs. KI₃ 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 O₂-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)–I₃⁻ reaction was not appreciably changed by increasing [MeCN] from 0.02 to 0.50 mol dm⁻³, or by adding GaCl₃ in concentration three times that of Ga^I.

Solutions of Ga(I) rapidly reduce I₃⁻, Br₂(aq), IrCl₆²⁻, HCrO₄⁻, Fe(CN)₆³⁻ and Fe(bipy)₃³⁺. Reduction of B_{12a} [aquacob(III)alamin] is slow, and there is no perceptible reaction with Co(NH₃)₅Cl²⁺ or Co(NH₃)₅Br²⁺. Each mol of Ga(I) consumes very nearly 1.0 mol of I₃⁻ or Br₂ but 2.0 mol of the

le⁻ oxidants IrCl₆²⁻ and Fe(bipy)₃³⁺, reflecting the expected conversion to Ga^{III} with oxidants of either type [eqn. (1) and (2)]:

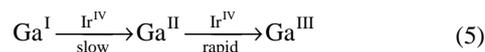


Oxidation by HCrO₄⁻ utilizes 0.64 ± 0.01 mol of Cr^{VI} in 0.01 M HClO₄ but 1.1 mol of oxidant when carried out in 2-ethyl-2-hydroxybutanoic acid buffer (EHBA/EHB⁻, pH 3.3), indicating predominant conversion to Cr^{III} in the absence of this chelating ligand [eqn. (3)] but formation of Cr^{IV} in its presence [eqn. (4)]:



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

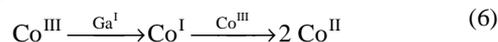
The reactions listed in Table 1 are first order in each of the redox partners. Although oxidations by IrCl₆²⁻ and Fe(bipy)₃³⁺ almost certainly pass through the intermediate state Ga^{II}, kinetic profiles for these oxidants exhibit no discontinuity attributable to the accumulation or decay of this odd-electron species, implying a two-step sequence (5), in which



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 s¹ intermediate, is much more strongly reducing than the parent s² 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 noted¹ for Ge^{II} (an isoelectronic state), Ga^I resists oxidation by both Co(NH₃)₅Cl²⁺ 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 4s² 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^o(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 shown¹¹ to undergo very rapid comproportionation with B_{12a} [eqn. (6)]:



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Notes and references

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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 (NaClO₄, 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

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

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