

Convenient preparation and improved stability of aqueous indium(I) solutions used in electron transfer reactions

Swapan K. Chandra* and Edwin S. Gould

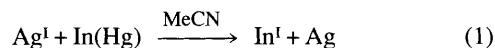
Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

Solutions 0.27 mol dm⁻³ in In^I, prepared by treatment of indium amalgam with silver triflate in dry acetonitrile, are stable for more than 5 days in the absence of oxygen and may be diluted 300-fold with water to give In^I(aq) solutions which are stable for over 5 h; kinetic patterns for reactions of [Co(NH₃)₅X]²⁺ (X = Cl⁻, Br⁻, I⁻, HC₂O₄⁻) with In^I point to a pair of consecutive 1 e transactions, the first (slower) of which is predominantly inner sphere.

Although scattered accounts of preparations of indium(I) in aqueous media have appeared,^{1,2} the procedures tend to be capricious and yield only low concentrations (≤ 3 × 10⁻⁴ mol dm⁻³) of In^I(aq).¹ Moreover, this oxidation state has been described³ as being quite unstable in aqueous solutions in the absence of high concentrations of halide.²

Here we report the preparation of aqueous indium(I) solutions having greater concentrations of this hypovalent centre than those previously recorded and exhibiting substantially improved stability. Such solutions have been used to compare the rates at which In^I reduces a series of one-electron oxidants derived from Co^{III}.

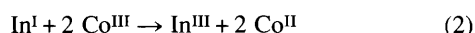
In a modification of the procedure of Headridge and Pletcher,³ a mixture of 12 g of Hg and 1.7 g of powdered In metal was heated at 180–190 °C for 1 h. This amalgamation, as well as all subsequent operations, was carried out under high purity (99.999%) argon. The indium amalgam was then cooled and stirred with a solution of 500 mg of dry silver triflate in 6 ml of dry acetonitrile for 12 h at 25 °C [eqn. (1)].



After separation from the precipitated Ag metal, [In^I] in the supernatant solution was found to be 0.27 mol dm⁻³ (spectrophotometric redox titration vs. KI₃ at 353 nm) and remained unchanged on standing for 5 days. Aqueous solutions for kinetics experiments, prepared by 300-fold dilution of the acetonitrile solution with O₂-free water, were stable for over 5 h in the absence of added electrolyte, as well as in acetate buffer (pH 4.5) and in 0.13 mol dm⁻³ LiClO₄, but decomposed slowly (17% loss in 5 min) in 0.06 mol dm⁻³ HClO₄.

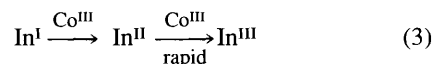
Indium(I) in the aqueous solutions used {[MeCN] = 0.07 mol dm⁻³} is taken to exist preponderantly as an aqua cation, since the rate at which In^I reduces [Co(NH₃)₅(N₃)₂]²⁺ (Table 1) is found to be unchanged when [MeCN] is increased from 0.07 to 1.0 mol dm⁻³.

The oxidation of In^I with [Co(NH₃)₅Cl]²⁺ yields 1.99 ± 0.03 moles of Co^{II} per mole of In^I. This conversion and, by implication, related reactions in the series, may then be represented by eqn. (2).



The In^I-Co^{III} reactions listed in Table 1 feature only one kinetic component, are first order each in the two redox partners, and proceed at rates independent of acidity in the range [H⁺] = 0.010–0.060 mol dm⁻³.

The observed kinetic picture, in conjunction with the 2:1 stoichiometry, is consistent with a two-step reaction sequence [eqn. (3)], proceeding through the metastable state In^{II}, which



reacts with Co^{III} much more rapidly than does In^I. The rate constants for the initial step would then be 1/2 of the tabulated values.

Rates of reduction with In^I are extraordinarily sensitive to structural modification. Among the halogeno-substituted oxidants, the iodo-chloro ratio (*k*_I/*k*_{Cl} = 660) is greater than that reported for all other metal-centred reductants except cob(II)alamin (vitamin B₁₂)⁴ and may be compared with the corresponding ratio (*k*_I/*k*_{Cl} = 20)⁵ pertaining to reductions by the outer-sphere reagent [Ru(NH₃)₆]²⁺. Since the model of Marcus⁶ stipulates that such ratios should be very nearly independent of the reductant for outer-sphere processes, this difference may be taken to imply the predominance of an inner-sphere (halide-bridged) path for the iodo oxidant.⁷ Analogous comparison of the ratio *k*_{Cl}/*k*_F (> 980) with that for the ruthenium(II) reductant (3.7)⁸ points to a bridged route for [Co(NH₃)₅Cl]²⁺ as well. Further evidence for the importance of redox bridging by O-donor ligands in indium(I) reductions is provided by the greater than 10³-fold acceleration when HC₂O₄⁻ is substituted for MeCO₂⁻ in the cobalt(III) oxidant. A rate enhancement of this type is most reasonably attributed to an increased degree of conversion to a Co^{III}-In^I precursor complex reflecting chelation of the indium centre by the oxalato function, an effect considered to be highly characteristic of inner-sphere processes.⁹

Table 1 Rate constants for oxidations of In^I by cobalt(III) complexes [Co(NH₃)₅X]²⁺^a

In ^I + 2 Co ^{III} → In ^{III} + 2 Co ^{II}	
Oxidant, [Co(NH ₃) ₅ X] ²⁺	<i>k</i> /dm ³ mol ⁻¹ s ⁻¹
X = F	≤ 0.008
Cl	7.9 ± 0.4
Br	(5.4 ± 0.5) × 10 ²
I	(5.2 ± 0.2) × 10 ³
N ₃	0.27 ± 0.03
NCS	0.09 ± 0.01
OAc	≤ 0.002
C ₂ O ₄ H	2.4 ± 0.2

^a Reactions at 25 °C in H₂O–MeCN (300:1); μ = 0.2 mol dm⁻³ (LiClO₄); [H⁺] = 0.01–0.06 mol dm⁻³. [In^I] = (7.8–8.2) × 10⁻⁴, [Co^{III}] = (4–12) × 10⁻³ mol dm⁻³. Conversions were monitored at the low-energy absorption maxima of the cobalt(III) oxidants. Rate constants pertain to the disappearance of Co^{III}; if the overall reaction is taken to proceed by eqn. (3), values of *k* for the initial electron transfer from In^I would be 1/2 of the tabulated values.

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

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Received, 4th December 1995; Com. 5/07868G