Contribution from the Department of Chemistry,
University of Windsor, Windsor, Ontario, N9B 3P4, Canada

Facile Synthesis of the Lower Halides of Indium

B. H. Freeland and D. G. Tuck*

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Many inorganic and organometallic syntheses rely on freshly prepared anhydrous metal halides as starting materials. Unfortunately, dehydration of the corresponding hydrates, either by heating in vacuo or by treatment with reagents such as thionyl chloride, often yields materials which are too inert, or too insoluble in organic solvents, for satisfactory handling.[1] The alternative direct high-temperature preparation of such anhydrous compounds from the elements suffers the additional disadvantages of inconvenient preparative scale and tedious procedure. All of these drawbacks apply in the case of the indium halides, since, until recently, the accepted routes to InX, InX_2, and InX_3 (X = Cl, Br, or I) involved high-temperature reactions.[2] In a recent publication, Gynane, Wilkinson, and Worrall[3] have reported a convenient synthesis of indium(III) iodide on the gram scale from the elements, using diethyl ether as the reaction medium. Analogous routes to the lower halides are obviously desirable, and we have now found that the use of aromatic solvents leads to such synthetic methods.

Indium metal reacts smoothly with iodine in refluxing aromatic solvents to form indium(III) iodide in high yield and good purity. Solutions of InI_3 in aromatic solvents react with excess indium metal under reflux with the gradual precipitation of pure, highly crystalline InI_2. The latter reaction is slow in benzene, but the use of the higher boiling xylenes results in a convenient reaction rate. Similar reductions may be effected in xylene with the tribromide or trichloride and excess indium metal.

On treatment of the dihalides with diethyl ether or other Lewis bases, the insoluble monohalide is precipitated and the corresponding trihalide–Lewis base adduct formed. The monohalides prepared in this manner are in a high state of subdivision and possess higher reactivity than do the fused materials obtained from sealed-tube experiments.[4]

Experimental Section

General Data. Analytical methods involved atomic absorption (indium) and argentometric titration (halides). Raman spectra, obtained with a Beckman 700 laser-Raman spectrometer (argon ion excitation at 488.0 nm), were compared with those reported earlier.[5] Solvents were distilled from sodium–benzophenone under nitrogen; reactions were carried out in a dry nitrogen atmosphere.

Preparation of Indium(III) Iodide. Indium shot (0.76 g, 6.6 mmol) was hammered into a thin foil and suspended in stirred degassed xylenes (80 ml). Iodine (2.52 g, 10 mmol) was added and the mixture refluxed until it appeared a pale yellow and all the indium metal had been consumed (about 1 hr). A crystal of iodine was then added and the solution again refluxed; the reaction was considered to be complete when refluxing for 15 min failed to discharge the color of the unreacted iodine. The xylene solution was filtered hot and allowed to cool to room temperature. The yellow plates which quickly separated were filtered off, washed with cold benzene (two 5-ml portions) to remove any traces of I_2, and dried in vacuo. Additional material separated on further cooling or on concentration of the solution in vacuo, raising the total yield to 3.1 g (94%). Anal. Calcd for InI_3: In, 23.2; I, 76.8. Found: In, 23.1; I, 76.8. Raman spectrum: 44 (m), 49 (m), 68 (m), 136 (vs), 192 (m), 225 (w) cm^{-1}.

Preparation of Indium Diiodide. (A) A solution of indium(III) iodide, prepared as above from In (1.24 g, 10.8 mmol) and I_2 (4.12 g, 16.2 mmol) in xylene (125 ml), was refluxed with excess indium foil (1.2 g) for 18 hr. Some yellow crystals precipitated at this point, and further yellow needles readily formed after slow cooling. These were collected and washed with dry, degassed, cold benzene (two 5-ml portions) and dried thoroughly in vacuo; yield 4.8 g (81%). Anal. Calcd for InI_2: In, 31.1; I, 68.9. Found: In, 31.2; I, 68.4; C, <0.1; H, <0.01. Raman spectrum: 47 (m), 67 (m), 141 (vs), 188 (m) cm^{-1}.

(B) InI (1.06 g, 4.4 mmol) was added to a solution of InI_3 (5.3 mmol, 20% excess) in xylene (100 ml) and the mixture refluxed. The red InI was gradually (few hours) converted to a yellow material as the yellow solution was decolorized. The final solid was treated as described in (A); yield 2.9 g (81%). Anal. Found: In, 31.2; I, 68.6.

Preparation of Indium(I) Iodide. Indium diiodide (1.41 g, 1.9 mmol) prepared by method (A) above was treated with diethyl ether (75 ml). On exposure to ether vapor, the yellow crystals immediately became deep red-purple, characteristic of InI. The suspension was stirred for a further 15 min and then filtered. The red powder was washed with diethyl ether (two 10-ml portions) and dried thoroughly in vacuo. Anal. Calcd for InI: In, 47.5; I, 52.5. Found: In, 47.6; I, 52.6. The combined filtrate and washings were evaporated to dryness in vacuo. The white solid which initially formed quickly turned yellow on warming in vacuo. The resulting yellow material was identified analytically and spectroscopically as InI_3.

Preparation of Indium Dibromide. The procedure was identical with that (A) described for InI_2 except that the product was sufficiently soluble in hot xylene to be filtered from any unreacted $InBr_3$ or indium metal through filter aid into a heated receiver. The long colorless needles which quickly precipitated on cooling were collected, washed with benzene, and dried in vacuo. Anal. Calcd for $InBr_2$: Br, 58.2. Found: Br, 57.9. Raman spectrum: 58 (m), 89 (m), 197 (vs), 234 (w) cm^{-1}.

Preparation of Indium Dichloride. The procedure again followed that described for InI_2 except that the reaction was slow and concentration of the mixture to small volume was necessary to effect complete reaction. The white product is almost insoluble in xylenes. Anal. Calcd for $InCl_2$: Cl, 38.2. Found: Cl, 37.9. Raman spectrum: 320 (w) cm^{-1}.

Preparation of Gallium(III) Iodide. The procedure was identical with that for InI_3. Anal. Calcd for GaI_3: I, 84.4. Found: I, 83.9.

Discussion

The initial indium–iodine reaction to yield InI_3 does not appear to call for any special comment, except that the method has one advantage over that of Gynane et al.[3] in that pyrolysis of a solvate is not required, since well-formed yellow crystals of InI_3 precipitate on cooling and are easily separated. We also note that the use of an aromatic solvent permits the direct synthesis of gallium(III) iodide. This compound cannot be obtained if ether is used as the reaction medium,[3] because of the formation of alkoxides during the thermolysis of the initially formed etherate $GaI_3 \cdot Et_2O$.

Analogous synthetic routes to $InBr_3$ or $InCl_3$ were investigated, but in both cases rapid attack on the aromatic solvent occurred. Efforts to form $InBr_3$ by bromination of $InBr_2$ in benzene were unsuccessful for similar reasons. Furthermore, although InI_3 in benzene reacts readily with bromine or chlorine to liberate iodine without appreciable solvent interferences, the indium(III) halides formed by this route retain significant and variable amounts of iodine. We have prepared $InBr_3$ by the bromination of indium metal in refluxing bromoform or ethylene dibromide, but the reactions are slow, and the products are judged of lower overall quality than those obtained by high-temperature methods.

Reaction Mechanism. The first step in the reduction of InI_3 by indium metal appears to be the production of the monoiodide on the surface of the metal, followed by its dissolution in the presence of the triiodide. In keeping with this, indium(I) iodide prepared from InI_3 and molten indium in a sealed-tube reaction is insoluble in aromatic solvents but readily reacts in these solvents on heating in the presence of InI_3 to yield InI_2. The overall reaction scheme for the iodide system may be described as follows; InI_2 is represented as the ionic dimer $In[InI_4]$ (see below) (B = Lewis base):

$$In + {}^{3}/_{2}I_2 \xrightarrow{\text{arene}} InI_3$$

$$InI_3 + 2In \rightarrow 3InI$$

$$InI + InI_3 \rightarrow In[InI_4]$$

$$In[InI_4] + B \rightarrow InI\downarrow + InI_3 \cdot B$$

The dihalides of indium are mixed oxidation state complexes,[5,6] and their ready formation in aromatic solvents seems worth further comment. Chao and Rieke[4] have prepared activated indium metal which forms InI quantitatively on reaction with iodine in refluxing xylene. We have observed that the amount of InI formed in the reduction of indium(III) iodide with commercial indium shot in xylene is insignificant until the formation of indium diiodide is well advanced, and the same is true even with molten indium in refluxing mesitylene. This inhibition may be due solely to deactivation of the surface of the indium metal by adhering InI, but it appears probable that complex formation with the aromatic solvent is important in stabilizing InX_2 in solution. Benzene solvates of gallium compounds have been reported,[7] and the formation of π complexes in solution has been proposed[8] in the case of gallium(I). It is reasonable to expect similar solvation of indium(I); the ion $[(\eta^6\text{-arene})In]^+$ would be isoelectronic with the well-known cyclopentadienylindium(I),[9] which involves a η^5 ligand.[10] The existence of such arene-indium complexes is currently under study, as are the reactions of these materials with a variety of unsaturated organic molecules.

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Registry No. InI_3, 13510-35-5; InI_2, 13779-78-7; InI, 13966-94-4; $InBr_2$, 14226-34-7; $InCl_2$, 13465-11-7; GaI_3, 13450-91-4; In, 7440-74-6; I_2, 7553-56-2; $InBr_3$, 13465-09-3; $InCl_3$, 10025-82-8; Ga, 7440-55-3.

References and Notes

(1) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, N.Y., 1965, p 72.
(2) See, for example, N. V. Sidgwick, "The Chemical Elements and Their Compounds", Vol. I, Oxford University Press, London, 1950.
(3) M. J. S. Gynane, M. Wilkinson, and I. J. Worrall, *Inorg. Nucl. Chem. Lett.*, **9**, 765 (1973).
(4) L. C. Chao and R. D. Rieke, *J. Organomet. Chem.*, **67**, C64 (1974).
(5) J. G. Contreras, J. S. Poland, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 922 (1973).
(6) A. J. Carty and D. G. Tuck, *Prog. Inorg. Chem.*, **19**, 245 (1975).
(7) J. G. Oliver and I. J. Worrall, *Inorg. Nucl. Chem. Lett.*, **3**, 575 (1967).
(8) E. Kinsella, J. Chadwick, and J. Coward, *J. Chem. Soc. A*, 969 (1968).
(9) E. O. Fischer and H. P. Hofmann, *Angew. Chem.*, **69**, 639 (1957).
(10) S. Shibata, L. S. Bartell, and R. M. Gavin, *J. Chem. Phys.*, **41**, 717 (1964).

Contribution from the Departments of Chemistry, State
University of New York, Stony Brook, New York 11794,
and Brookhaven National Laboratory, Upton, New York 11973

Temperature-Jump Study of the Reaction between Hexacyanoferrate(II) and -(III) and Tris(phenanthroline)cobalt(II) and -(III)

Albert Haim*[1a] and Norman Sutin*[1b]

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Most studies of outer-sphere redox reactions of metal ions and their complexes have been carried out with ions of the same charge type.[2a] Under these circumstances, the rate measurements yield second-order rate coefficients which are products of the equilibrium constant for the formation of the precursor complex (eq 1) and the rate constant for the

$$\text{Ox} + \text{Red} \rightleftharpoons \text{Ox}\|\text{Red} \quad Q_\text{p} \tag{1}$$

electron-transfer step (eq 2). By using highly charged

$$\text{Ox}\|\text{Red} \rightarrow \text{Ox}^- + \text{Red}^+ \quad k_\text{et} \tag{2}$$

reactants of opposite charge, it has been proved possible to resolve an observed rate coefficient into its elementary components.[2b]

Table I. Equilibrium Quotient for Reaction 3[a]

$10^3[Fe(CN)_6^{4-}]_0$, *M*	$10^4[Fe(CN)_6^{3-}]_0$, *M*	$10^4[Co(phen)_3^{3+}]_{eq}$,[b] *M*	*Q*
0.86	5.30	3.96	5.8
1.01	5.04	3.54	4.7
2.01	5.04	3.05	4.9
2.14	5.30	4.28	5.0[c]
4.73	5.09	2.22	4.7
4.79	5.08	2.20	4.7
9.46	5.09	1.64	5.3
9.58	5.08	1.69	5.7
15.2	5.01	1.20	5.3
20.3	5.01	0.80	4.0
2.01	4.81	3.92	16.5[d]

[a] At 25°, [phen] = 0.010 *M*, $[KNO_3] = 0.10$ *M*, and $[Co(phen)_3^{2+}]_0 = 1.03 \times 10^{-3}$ *M*. [b] From eq 4. [c] $[Co(phen)_3^{2+}] = 2.59 \times 10^{-3}$ *M*. [d] At 15°.

The present study was initiated with the expectation of obtaining Q_p and k_et for the $Co(phen)_3^{3+}$–$Fe(CN)_6^{4-}$ reaction. This expectation was not realized, but the results still show the importance of electrostatic factors in determining rates of outer-sphere reactions as well as the need to consider carefully the nature of the coordination sheres of metal ions in the estimation of ion-pair formation constants.

Experimental Section

Materials. Triply distilled water was used in the preparation of all of the solutions. All chemicals used were of the highest quality available and were used as received.[3] The ion $Co(phen)_3^{2+}$ was prepared in situ by the reaction of $Co(NO_3)_2$ with excess phenanthroline.

Equilibrium Measurements. The equilibrium quotient for reaction

$$Fe(CN)_6^{3-} + Co(phen)_3^{2+} \rightleftharpoons Fe(CN)_6^{4-} + Co(phen)_3^{3+} \quad Q \tag{3}$$

3 was determined by a spectrophotometric technique. Following chemical and temperature equilibrium, the absorbance *A* of solutions containing the desired concentrations of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Co(phen)_3^{2+}$ was measured at 420 nm, the wavelength for maximum absorption by $Fe(CN)_6^{3-}$. The concentration of $Co(phen)_3^{3+}$ at equilibrium was calculated from the expression

$$[Co(phen)_3^{3+}]_{eq} = \frac{A - (A_1 + A_2 + A_3)}{\epsilon_1 - \epsilon_2 - \epsilon_3 + \epsilon_4} \tag{4}$$

where A_1, A_2, and A_3 (measured for each experiment) are the absorbances of solutions of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$ at concentrations equal to the initial concentrations (i.e., before equilibration), and ϵ_1, ϵ_2, ϵ_3, and ϵ_4 are the molar absorptivities at 420 nm of $Fe(CN)_6^{4-}$ (2), $Fe(CN)_6^{3-}$ (1026), $Co(phen)_3^{2+}$ (126), and $Co(phen)_3^{3+}$ (139), respectively. The equilibrium quotient for reaction 3 was then calculated from the known initial concentrations of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$ and the calculated equilibrium concentration of $Co(phen)_3^{3+}$.

Kinetic Measurements. The temperature-jump apparatus described previously[4] was used. The cell (equipped with gold electrodes) was filled with the solution containing the desired concentrations of $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, and $Co(phen)_3^{2+}$, as well as 0.10 *M* potassium nitrate as supporting electrolyte, and then placed in a constant-temperature bath. The condenser was discharged through the solution, bringing the temperature to 25°, and the chemical relaxation was followed spectrophotometrically at 420 nm. Transmittance vs. time oscillograms were photographed, and relaxation times were calculated from the log *T* vs. *t* linear plots.

Results and Discussion

The values of the equilibrium quotient for reaction 3 are presented in column 4 of Table I. The average value 5.0 ± 0.4 at 25° and $[KNO_3] = 0.10$ *M* is in satisfactory agreement with the value 1.0 calculated from the reduction potentials for the $Fe(CN)_6^{3-,4-}$ and $Co(phen)_3^{3+,2+}$ couples.[5,6] From the average value $Q = 5.0$ at 25° and the single measurement at 15° (16.5), we calculate $\Delta H° = -20 \pm 3$ kcal mol^{-1} and $\Delta S° = -65 \pm 10$ eu. The negative values for $\Delta H°$ and $\Delta S°$ appear