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Reinvestigation of the Reaction of Samarium Metal with Mercury(II) Iodide

Glen B. DEACON * and Craig M. FORSYTH
Chemistry Department, Monash University,
Clayton Victoria 3168, Australia

Samarium(II) iodide is obtained from reaction of mercury(II) iodide with an excess of samarium metal in boiling tetrahydrofuran. The preparation involves formation and reduction of samarium(III) iodide and is affected by the quality of the samarium metal.

The recent report [1] that samarium triiodide is reduced to the diiodide by metallic samarium in tetrahydrofuran (thf) is at variance with our earlier isolation of $SmI_3(thf)_3$[2,3] from reaction of samarium metal with mercury(II) iodide (mole ratio 1.1:1.0) in boiling thf, <u>despite</u> use of a stoichiometry appropriate for SmI_2 formation.

$$3HgI_2 + 2Sm \xrightarrow{thf} 2SmI_3(thf)_3 + 3Hg\downarrow \quad (1)$$

In an attempt to resolve this problem, we have reinvestigated the Sm/HgI_2 reaction with attention to metal quality. Factors relating to the synthesis of SmI_2 and the relative stabilities of SmI_2 and SmI_3 are important in view of the extensive uses of SmI_2 as a reductant in organic synthesis [4] and as a key reagent in the preparation of samarium(II) organometallics.[5]

Reaction of mercury(II) iodide with an excess of good quality samarium powder (mole ratio, 1.0 : 2.1) under purified nitrogen in refluxing thf [6a] gave a yellow (SmI_3) and grey (Hg) suspension in 0.5 h. A blue-green colour (SmI_2) then developed and was intense in 1 h. After heating for 22 h. the reaction mixture was filtered to remove mercury and the excess of samarium, and $SmI_2(thf)_2$ (72%) was obtained on evaporation of the filtrate.[6a]

$$HgI_2 + Sm \xrightarrow{thf} SmI_2(thf)_2 + Hg\downarrow \quad (2)$$

A larger scale reaction with a lower Sm:Hg ratio (1.4:1.0) gave a 91% yield after refluxing for 72 h.[6b] When the reaction was repeated on the reported [2] scale (see above),[6c] initial formation of SmI_3 followed by SmI_2 was again observed. Filtration after 8 h. removed some SmI_3 as well as mercury, and $SmI_2(thf)_2$ (77%) was isolated from the filtrate. Use of metal powder that had been exposed to air [6d] in a reported scale [2] reaction [6c] gave a green solution containing suspended SmI_3 after 2 h, and some triiodide remained after refluxing for 48 h.

Thus, $SmI_2(thf)_2$ can be prepared in good yield from Sm and HgI_2, provided a sufficient excess of good quality metal is used, and the method is competitive with alternative syntheses.[1,4,5,7,8] Reaction (2) involves initial formation of the previously isolated $SmI_3(thf)_3$ [reaction (1)] followed by reduction[1] with samarium metal. The earlier isolation of $SmI_3(thf)_3$[2] is attributable to use of poor quality metal powder [6d] and a shorter reaction time than used for reaction (2).

References

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6)a) Sm powder (Research Chemicals; handled and stored in a dry box under purified N_2) (5.99 mmol) and HgI_2 (2.88 mmol) in boiling thf (35 ml) gave $SmI_2(thf)_2$ (Found: Sm, 27.5. Calc.: Sm, 27.4%) with visible/near i.r. absorption in agreement with that reported.[7] b) Sm (16.6 mmol), HgI_2 (12.0 mmol), thf (120 ml). c) Sm (3.06 mmol), HgI_2 (2.88 mmol), thf (25 ml). d) The sample of metal powder had been exposed to air several times and was not stored or handled under N_2.

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