

Novel reducing properties of a series of lanthanoid metals in the presence of SmI₂

Yuri Tomisaka · Aya Yoshimura · Akihiro Nomoto ·
Motohiro Sonoda · Akiya Ogawa

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Abstract The reduction of dodecyl iodide, as model compound, with a series of lanthanoid (Ln) metals in the presence of catalytic amounts of samarium diiodide (SmI₂) has been investigated in detail. The reducing activity of SmI₂/Ln and the kinds of reduced products were found to be dependent on the individual Ln, but not on SmI₂.

Keywords Lanthanoid metal · Samarium diiodide · Relative reducing activity · Reduction · Alkyl iodide

Introduction

Samarium diiodide (SmI₂) is widely used as a mild, single-electron reducing reagent in organic synthesis [1–12].¹ SmI₂ is soluble in tetrahydrofuran (THF; concentration up to 0.1 M), and, owing to its homogeneous nature, reduction of organic compounds with SmI₂ is cleaner than with other heterogeneous single-electron reducing reagents. Although SmI₂ is commercially available as its THF solution, it can be prepared easily by reaction of samarium (Sm) metal with 1,2-diiodoethane in THF [13]. In this preparation process, Sm metal consumes two electrons to form divalent SmI₂. Owing to the stability of trivalent lanthanoids, one residual electron

¹ SmI₂ is a useful reagent in organic synthesis, see, for example, Ref. [1].

Y. Tomisaka · A. Yoshimura · A. Nomoto · M. Sonoda · A. Ogawa (✉)
Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan
e-mail: ogawa@chem.osakafu-u.ac.jp

Y. Tomisaka
Advanced Materials Research Laboratory, KRI, Inc., Kyoto Research Park, 134 Chudoji Minami-
machi, Shimogyo-ku, Kyoto 600-8813, Japan

is used for reduction of organic molecules. If Sm metal and other Ln metals are directly used for reducing organic molecules, all three electrons of these Ln metals can be used efficiently. However, both coating of the surface of Ln metals with air (molecular oxygen) and/or moisture (water) and the heterogeneous nature of Ln metals in organic solvents contribute to the difficulty in efficiently reducing organic molecules by use of Ln metals. Therefore, several methods for the activation of Ln metals have been proposed: for example, treatment with small amounts of iodine (I₂) [14], sonication [15–18], photoirradiation [19, 20], and the use of *N,N*-dimethylformamide as solvent [21–24].

Recently, we have developed two novel reduction systems based on SmI₂, an SmI₂–Sm mixed system and an SmI₂–*hν* system. In the former system, the mixture of divalent and zerovalent samarium species has greater reducing activity than the corresponding single systems [25–30]. In the latter system, visible-light irradiation substantially enhances the reducing activity of SmI₂ [31–40].² We have, furthermore, investigated the reducing activity of a series of rare earths when photoirradiated [42]. Photoirradiation was found to be effective in reducing alkyl halides by use of several Ln metals, for example cerium (Ce), neodymium (Nd), Sm, and europium (Eu) [19]. Unfortunately, however, other rare earth metals, when photoirradiated, did not reduce alkyl halides. The corresponding divalent species of Ce, Nd, Sm, and Eu (LnI₂, Ln = Ce, Nd, Sm, and Eu) are, to some extent, soluble in THF, different from other rare earths. Thus, combination of SmI₂ with a series of rare earth metals is promising, because SmI₂ forms a homogeneous solution in THF. Herein we report the reducing activity of novel combinations of SmI₂ with a series of rare earth metals, using dodecyl iodide (**1**) as model compound.

Experimental

Instruments

Gas chromatography (GC) was performed with a Shimadzu GC-14A instrument equipped with a flame ionizing detector and a capillary column (CPB1, 0.25 mm x 30 m, 250 °C). Yields of the reduced products, dodecane (**2**), tetracosane (**3**), and 1-dodecene (**4**), on the basis of the starting material (1-iodododecane, **1**), were determined by GC analysis. The standard reagents **1**, **2**, **3**, and **4** were purchased from TCI (**1**: 4292-19-7, **2**: 112-40-3, **3**: 646-31-1, **4**: 112-41-4); their retention times were 15.3, 8.4, 43.8, and 8.0 min, respectively.

General comments

Powders of rare earths except Eu were purchased from commercial sources (40 mesh, 99.9 % in mineral oil) and were used after washing with dry *n*-pentane, to remove the mineral oil, followed by drying for 3 h under reduced pressure. Eu

² A THF solution of SmI₂ has a deep blue color with absorption maxima at 565 and 617 nm, which can be assigned to a $4f^6 \rightarrow 4f^5 5d^1$ transition [32].

powder was obtained by powdering (ca 20 mesh) an Eu ingot (99.9 %) in a grove box under a nitrogen atmosphere. Before use, THF was distilled from sodium/benzophenone ketyl under a nitrogen atmosphere.

Preparation of SmI₂/Ln reagents

Rare earth (Ln: mesh size ca 40 mesh except Eu, ca 20 mesh) powder (0.8 mmol), Sm powder (0.2 mmol), 1,2-diiodoethane (0.2 mmol), and freshly distilled THF (2 mL) were placed in a three-necked flask equipped with a reflux condenser and a dropping funnel. The mixtures were stirred for 1.5 h at room temperature; the color of the solution changed to dark blue (Scheme 1).

Reduction of dodecyl iodide with SmI₂/Ln reagent

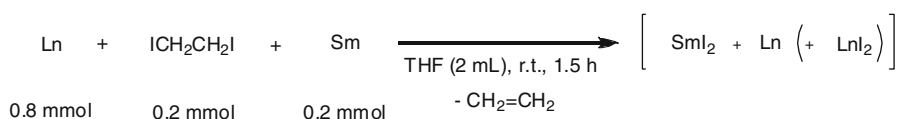
A solution of **1** (0.5 mmol), 2-PrOH (2.0 mmol), and tetradecane as internal standard in THF (2 mL) was added dropwise to the resulting THF solution of SmI₂/Ln for 1 h, and reaction was continued for an additional 2 h. The flask was exposed to air to quench the reaction, and then saturated NaHCO₃ aqueous solution was added to the mixture. After extraction of the products with ether, the combined extract was dried (MgSO₄), and analyzed by GC.

Results and discussion

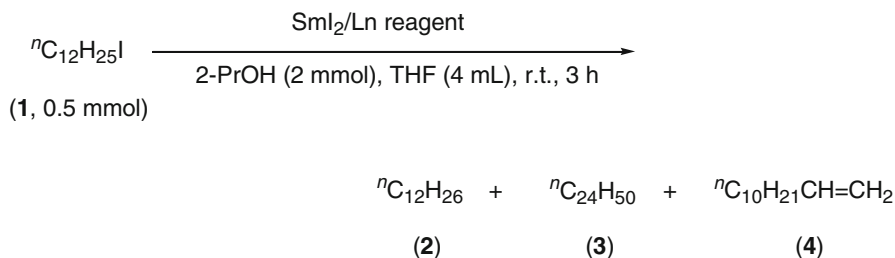
First, we prepared the SmI₂/Ln reagent (Scheme 1). A mixture of the appropriate Ln metal powder (0.8 mmol), Sm powder (0.2 mmol), and 1,2-diiodoethane (0.2 mmol) in THF (2 mL) was stirred at room temperature for 1.5 h under nitrogen atmosphere. After stirring, the color of the solution changed to dark blue. This observation clearly indicates the generation of SmI₂ [13] because other divalent rare earth species do not have this blue colour. Unreacted Ln metal remained insoluble in THF (Scheme 2).

A mixture of **1** (0.5 mmol), as model compound, and 2-PrOH (2.0 mmol), as proton source, in THF (2 mL) was dropped into the prepared SmI₂/Ln reagent in THF. After the reaction, the resulting products were analyzed by GC. The results are summarized in Table 1.

With scandium (Sc) and yttrium (Y), reduction of **1** with the SmI₂/Ln reagent did not proceed. Sc and Y are Group 3 transition metal elements; however, they do not have a 4*f*-orbital electron. Lutetium (Lu), also, had no reducing activity in the



Scheme 1 Preparation of SmI₂/Ln reagent



Scheme 2 Reduction of dodecyl iodide (**1**) with SmI₂/Ln reagent

Table 1 Reduction of dodecyl iodide (**1**) with SmI₂/Ln reagents

Yield (%)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2	0	0	92	93	93	89	86	42	53	57	42	35	22	6	53	0
3	0	0	2	1	1	1	2	0	24	1	0	0	0	0	24	0
4	0	0	2	2	0	0	0	0	3	1	0	0	0	0	3	0

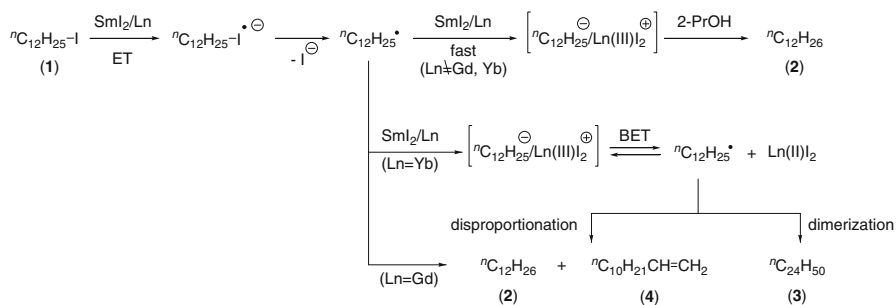
presence of SmI₂. All 4*f*-orbitals of Lu are fully occupied by electrons, and therefore, Lu is very stable and less reactive.

Except for Sc, Y, and Lu, the mixed systems comprising the combination of other rare earth metals and SmI₂ had reducing activity in reduction of **1**. In particular, with the light rare earth elements (LREE), lanthanum (La), Ce, praseodymium (Pr), Nd, Sm, and Eu, reduction of **1** proceeded efficiently to yield **2** selectively. In contrast, the reducing activity of heavy rare earth elements (HREE), for example terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and thulium (Tm), were lower than that of LREE, and the yields of dodecane decreased in proportion to the increase in atomic number. In the initial stage of the reaction, the strong affinity of Sm for oxygen might have induced reduction of the oxide-coated metal surfaces.³

It is worthy of note that the SmI₂/gadolinium (Gd) and SmI₂/ytterbium (Yb) reagents had somewhat different reactivity. In both cases, **3** and **4** were formed besides **2** (e.g., yield of **3**: 24 % (Gd), 24 % (Yb)). Gd is known as the inflection point in the physical and chemical properties of the rare earth elements [43]. These phenomena are explained reasonably well by the electronic state of Gd, which has unpaired electrons in all of its 4*f*-orbitals. On the other hand, Yb is a single-electron-deficient element from the closed shell of Lu, and therefore, on the basis of the driving force preferred by Yb to obtain a single electron, specialized properties and reactivities are sometimes observed.

In a series of reduction systems using SmI₂/Ln reagents, if only SmI₂ acts as a reducing agent and Ln metals solely regenerate SmI₂, the results of reduction would

³ Most divalent species of Ln (LnI₂) except SmI₂ are less soluble in organic solvents, and, therefore, reduction of the oxidized surface of Ln metals with LnI₂ is inefficient. In contrast, SmI₂, which is soluble in THF, can efficiently reduce the oxidized surface of Ln metals. The reducing potential of SmI₂ is –1.55 eV, whereas Ln metals have higher reducing potentials (–2.23 to –2.48 eV). Therefore, SmI₂/Ln generally had greater reducing activity than LnI₂/Ln.



Scheme 3 A possible pathway for reduction of dodecyl iodide (1)

be similar to each other. Very interestingly, however, the above-mentioned results clearly indicate the characteristic features of individual rare earth elements.

A possible pathway for the reduction of **1** using the SmI₂/Ln reagent is shown in Scheme 3. Compound **1** undergoes electron transfer (ET) from the SmI₂/Ln species to yield the corresponding dodecyl radical, which is reduced to a dodecyl anion species by another SmI₂ (or SmI₂/Ln).^{4,5} Protonation of the dodecyl anion species affords **2**. On the other hand, **3** and **4** are obtained by dimerization and disproportionation, respectively, of the dodecyl radical. With SmI₂/Gd and SmI₂/Yb, the dimerization and disproportionation reactions proceeded as side-reactions. Owing to the instability of GdI₂, the concentration of GdI₂ in THF was lower than for other divalent rare earth diiodides. This probably enables dimerization and disproportionation of the dodecyl radicals (ⁿC₁₂H₂₅[•]) before reduction to the dodecyl anion species. The divalent state of Yb is stable, and, therefore, there may have been a reverse process of [ⁿC₁₂H₂₅⁻/Ln(III)I₂⁺] to Ln(II)I₂ and ⁿC₁₂H₂₅[•] by back electron transfer (BET). This probably contributed to the efficiency of dimerization and disproportionation of ⁿC₁₂H₂₅[•].

Conclusion

In summary, we have systematically investigated the generation and reducing activity of a series of SmI₂/Ln reagents. In general, the reactivity of a series of rare earths changes at *f*⁶ (Eu) or *f*⁷ (Gd) which are half-filled lanthanides. Synthetic use of HREE has been achieved in this reaction system, although the reactivity of systems using LREE is higher than those using HREE. These results strongly suggest that the electronic states of rare earth elements affect the reducing activity of the SmI₂/Ln reagents. The SmI₂/Ln reagents make it possible to use three electrons of Ln metals for reductive transformations.

⁴ When SmI₂ was used without Ln, 8 % of **2** was obtained; Ref. [42].

⁵ Most of the unreacted starting material (**1**) was recovered. Formation of dodecyl anion was confirmed by quenching with ketone (Barbier reaction); Ref. [26].

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