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# Electrochemical Investigation of the Reducing Power of $SmI_2$ in THF and the Effect of HMPA Cosolvent

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**Abstract:** The reduction potential of $SmI_2$ in THF is reported. The effect of varying concentrations of HMPA on the redox potential was determined employing linear sweep voltammetry (LSV). These data show the utility of electrochemistry in studying synthetically important reducing reagents.

One of the most important and exciting recent developments in organic chemistry has been the evolution of samarium diiodide ($SmI_2$) for use in synthesis.[1] There are essentially three types of transformations mediated by $SmI_2$; functional group reductions, reductive coupling of $\pi$ bonds, and reductive coupling of halides and $\pi$ bonds.[2] A number of redox potentials have been cited for $SmI_2$ in the recent literature,[3] but inspection of the primary literature for these sources reveals that the redox potentials are for samarium(III) perchlorate in propylene carbonate[4] and acetonitrile[5] respectively. The ability of Sm(II) to coordinate many ligands (including solvent) suggests that the redox potential of a divalent Sm species will vary depending on the types of ligands bound to it, and the solvent milieu.[6] Inanaga discovered that the addition of HMPA to $SmI_2$ in THF increased the rate of carbon halogen bond cleavage.[7] This discovery led to a number of preparative advances, especially involving the reductive coupling of halides and $\pi$ bonds. Although there are numerous synthetic examples[2a, b] of the ability of HMPA to increase the redox potential of $SmI_2$, no quantitative data have been forthcoming. The change in the redox potential of the reducing agent may significantly alter the mechanism of a reaction, possibly with deleterious effects. Determination of the redox potential of $SmI_2$ in THF and the effect of HMPA will allow insight into the energetic changes that occur with changes in cosolvent concentration. Species that are not reduced by $SmI_2$ alone may be reduced by the $SmI_2$-HMPA complex. In this letter, we report our electrochemical studies of the reducing power of $SmI_2$ in THF, and the effect of HMPA cosolvent on the reducing power of $SmI_2$ as a function of concentration.

Electrochemistry is an excellent tool to study the energetics of single electron transfer and in general, organic chemists have underutilized this simple, reliable technique. The oxidation potential of $SmI_2$ in THF was determined using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). The concentration of $SmI_2$ in all of the electrochemical experiments performed in this study was 0.5 mM. The working electrode employed was a standard glassy carbon electrode and a platinum wire was used as the auxiliary electrode. A silver/silver nitrate electrode was used as a reference.[8] The choice of electrolyte is critical for these experiments. Tetraalkylammonium electrolytes containing perchlorate and tetrafluoroborate counterions tended to coordinate with the $SmI_2$. The addition of tetrabutylammonium tetrafluoroborate changed the blue $SmI_2$ solution to a deep red color. The addition of tetrabutylammonium perchlorate had the same effect. Examination of the UV-vis spectra of $SmI_2$ containing electrolytes with either perchlorate or tetrafluoroborate counterions showed large shifts in the $SmI_2$ bands at 552 and 616 nm. These results indicate that either the perchlorate and tetrafluoroborate counterions were coordinating to the $SmI_2$ or they were displacing the iodide ligands on the samarium. After examining a number of electrolytes, we determined that tetrabutylammonium hexafluorophosphate was a reasonable electrolyte. This electrolyte did not change the color of the $SmI_2$ solution and inspection of the UV-vis spectrum showed no changes of the peaks contained in the UV or visible region. The redox potential of $SmI_2$ in THF (employing the tetrabutylammonium hexafluorophosphate 0.1M) was determined to be -1.33 ± 0.01 V vs. the $Ag/AgNO_3$ reference electrode.

The effect of HMPA concentration on the oxidation potential of $SmI_2$ in THF was studied by adding successive one equivalent amounts of HMPA to $SmI_2$ and recording a linear sweep voltammogram for each cosolvent addition. Table 1 contains the measured oxidation potentials vs the $Ag/AgNO_3$ reference electrode for 0 to 6 equivalents of HMPA cosolvent.

**Table 1. Effect of HMPA on the Oxidation Potential of $SmI_2$.**

| Entry | Equivalents of HMPA vs. $SmI_2$[a] | Oxidation Potential, V[b] | ΔE, V (kcal) |
|---|---|---|---|
| 1 | 0 | -1.33 | 0 |
| 2 | 1 | -1.43 | 0.10 (2.3) |
| 3 | 2 | -1.46 | 0.13 (3.0) |
| 4 | 3 | -1.95 | 0.62 (14.0) |
| 5 | 4 | -2.05 | 0.72 (16.6) |
| 6 | 5 | -2.05 | 0.72 (16.6) |
| 7 | 6 | -2.05 | 0.72 (16.6) |

a) concentration of $SmI_2$ = 0.5 mM. b) vs. $Ag/AgNO_3$ reference electrode in THF.

Addition of up to 2 equivalents of HMPA to $SmI_2$ showed only a small shift in the oxidation potential of the reducing agent equivalent to approximately 3 kcal. The addition of 3 equivalents of HMPA to $SmI_2$ had a drastic effect on the redox potential, effectively increasing the oxidation potential from -1.33 V to -1.95 V. This change of 0.62 V is equivalent to an increase of 14 kcal in the reducing power of the $SmI_2$-HMPA species. The addition of 4 equivalents of HMPA to $SmI_2$ increased the potential even further to -2.05 V. Further addition of HMPA showed no effect on the redox potential. The linear sweep voltammograms for $SmI_2$, $SmI_2$ containing 2 equivalents of HMPA, and $SmI_2$ containing 4 equivalents of HMPA are displayed in Figure 1. The linear sweep voltammogram of $SmI_2$ containing 2 equivalents of HMPA is interesting because it displays two peaks. The major peak is at -1.46 V and the second is at -1.80 V. It appears that there are at least two species being oxidized in this experiment. It would seem reasonable to surmise that the two peaks correspond to $SmI_2$ and HMPA ligated $SmI_2$, however, the exact speciation in solution cannot be determined from this experiment.

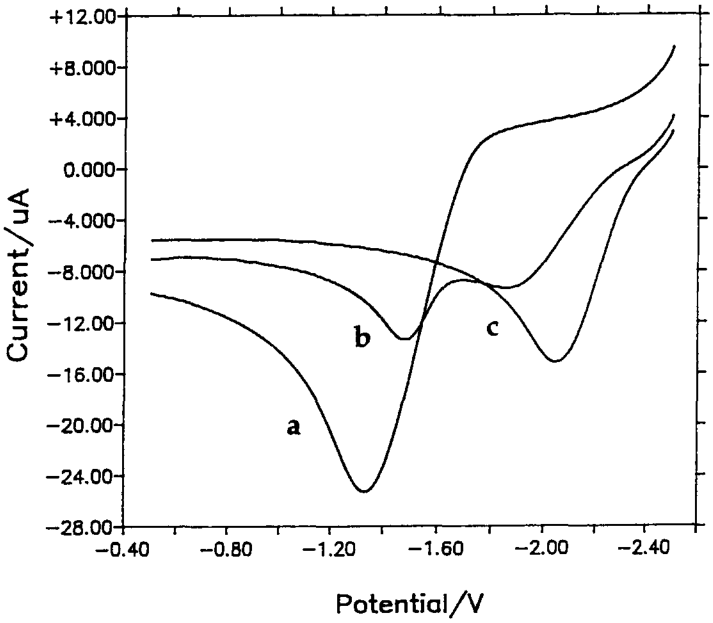

Figure 1. a) The LSV (anodic peak current) of $SmI_2$ at a glassy carbon electrode in THF vs $Ag/AgNO_3$ reference electrode. b) LSV of $SmI_2$ containing 2 equivalents of HMPA. c) LSV of $SmI_2$ containing 4 equivalents of HMPA.

Although we have been unable to find any other quantitative data concerning the effect of HMPA on the redox potential of $SmI_2$, these results are consistent with two other recent studies concerning the use of HMPA as a cosolvent. In 1993, Hasegawa and Curran[9] studied the rate constants for the reactions of primary alkyl radicals with $SmI_2$ at different HMPA concentrations employing 6-iodo-1-hexene as a radical clock. They observed that the reaction time of 6-iodo-1-hexene containing $SmI_2$ without HMPA was too slow for their rate experiments. They found that measurable reaction times were attained with 2 equivalents of HMPA and that the rates increased on addition of up to five equivalents of HMPA. These kinetic data correlate reasonably well with our redox potential data. $SmI_2$ containing 2 equivalents of HMPA contains a species with a redox potential high enough to cleave a carbon-iodine bond.[10] While we see no change in the oxidation potential of the $SmI_2$-HMPA species above 4 equivalents of HMPA, Curran[9] observed a further rate increase with 5 equivalents of HMPA. In 1994, Hou and coworkers[11] successfully isolated and structurally characterized the complex $SmI_2(HMPA)_4$. Our observation that increasing the amount of HMPA above 4 equivalents shows no effect on the oxidation potential of $SmI_2$ is consistent with the structure determined by Hou being the reactive intermediate responsible for the unique reactivity of the $SmI_2$-HMPA complex.

The electrochemical experiments contained in this letter give important energetic information concerning the reducing power of $SmI_2$ and $SmI_2$ containing varying concentrations of HMPA. The combination of these energetic data with the known reduction potentials of carbon-halogen bonds and carbonyls may give insight into the mechanisms of a number of reductive coupling reactions mediated by $SmI_2$. These experiments also show the importance of careful choice of electrolyte for electrochemical measurements to determine the redox potential of a structurally well defined lanthanide. The redox potentials of other divalent samarium compounds, the effect of solvent and cosolvent on the redox potential and the importance of all of these variables on reactivity will be presented in a forthcoming paper.

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