Experimental Procedures

THF was distilled from sodium benzophenone ketyl, under nitrogen. All solvents employed in this study were degassed by several cycles of evacuating the vessel and refilling with nitrogen. Small amounts of water were found to have a deleterious effect on the reactions and electrochemistry, therefore all cosolvents were dried by vacuum distillation from NaOH pellets or $MgSO_4$. Distilled THF and HMPA were checked by Karl Fischer titration. Dried solvents and salts were stored in an Innovative Technology, Inc. drybox containing a nitrogen atmosphere and a platinum catalyst for drying.

The redox potentials of SmI_2 and the SmI_2-additive mixtures in THF were measured by cyclic voltammetry employing a BAS 100B electrochemical analyzer. The working electrode was a standard glassy carbon electrode. The electrode was polished with 0.05mm polishing alumina or cleaned in an ultrasonic bath. The electrode was rinsed with acetone or ethanol and dried before each run. The auxiliary electrode was a platinum wire. The SCE was used as a reference electrode. The electrolyte employed in all experiments was either tetrabutylammonium hexafluorophosphate or LiI. The concentration of SmI_2 in all of the electrochemical experiments was 0.5 mM. All solutions were prepared in the drybox and transferred to the electrochemical analyzer for analysis.

Electrochemistry

The influence of HMPA on the redox potential of SmI_2 was studied by adding successive one equivalent amounts of additive and recording a CV. The experimental conditions were as follows:

Inititial E (mV) = -2600

Final E (mV) = -500

Sweep rate (mV/s) = 100

Quiet T (s) = 2

Sensitivity (A/V) = 1 E-5

Digital Simulations

Digisim 2.1 (Bioanalytical Systems Inc.) was used for simulation of the experimental voltammograms. The parameters for the simulated voltammogram of SmI_2 are the same values reported in reference 9. A sweep rate of 100mV was used in the simulation to match the experimental sweep rate. The value of α employed was 0.5.

Marcus Theory

The reorganization energy, λ for the electron transfer is determined from the average of the reorganization energies of the oxidant and reductant. Both Saveant[1] and Lund[2] have estimated the λ for an alkyl radical to be approximately 50 kcal/mol. We estimated a λ for the SmI_2 $(HMPA)_4$ complex to be approximately 30 kcal/mol. The λ for the electron transfer from the $SmI_2(HMPA)_4$ complex to a primary alkyl radical is roughly 40 kcal/mol. We estimate that the error may be as high as 10%. The error in λ and the experimental error in the redox potentials were propagated through the Marcus equation to provide a value of $3 \pm 1 \times 10^6$ $M^{-1}s^{-1}$ for outer-sphere ET.

1. Saveant, J.M.; Gallardo, I.; Andieux, P.C. *J. Am. Chem. Soc.* **1989**, *111*, 1620.
2. Occhialini, D.; Pedersen, U.S.; Lund, H. *Acta Chem. Scand.* **1990**, *44*, 715.