

The Effect of Cosolvent on the Reducing Power of SmI_2 in Tetrahydrofuran.

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Received 17 March 1998; accepted 14 April 1998

Abstract The influence of additives on the reducing power and reactivity of samarium(II) iodide is presented. Different cosolvents (ligands) employed in SmI_2 mediated reactions have different affinities for SmI_2 in THF. Cosolvent concentration is an important factor in determining the reducing power of the Sm(II) -cosolvent complex. © 1998 Elsevier Science Ltd. All rights reserved.

The emergence of divalent lanthanides (especially SmI_2) as reagents in synthesis has had a profound influence on the way organic chemists construct carbon-carbon bonds via the reductive coupling of π bonds, and the reductive coupling of halides and π bonds. The elegant work of Molander¹ and others²⁻⁴ illustrates the unique reactivity and selectivity of SmI_2 . The addition of HMPA cosolvent to SmI_2 -mediated reductive bond couplings has a drastic effect on the rates of these reactions.⁵ Other cosolvents containing basic oxygen, including 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU)^{1d, 6} and 1,1,3,3-tetramethylurea (TMU)⁷ have been employed in synthetic applications. Recently, a number of other divalent samarium species including samarium dibromide⁸ and samarium(II)triflate⁹, have emerged as useful reductive coupling agents. 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. This supposition implies that it may be possible to “fine tune” the redox potential of a divalent Sm reducing species by making changes in both the cosolvent, and the ligands attached to the Sm . The ability to selectively modify the redox potential of a reducing species simply by adding a cosolvent could have significant ramifications in the synthesis of complex molecules containing a number of reducible functionalities. Although numerous cosolvents have been employed with SmI_2 , there have been no attempts to quantify (in terms of reducing power) the effect of these additives on the oxidation potential of SmI_2 or other divalent Sm species. The structure and reducing power of the Sm(II) -cosolvent complex should have a profound influence on the reactivity of the reducing reagent. In this communication, we report the effect of cosolvent and its concentration on the oxidation potential of SmI_2 in THF.

We set out to examine cosolvents that were reported to increase the rates of reductive coupling reactions mediated by SmI_2 in THF. Experimental descriptions of a number of SmI_2 -cosolvent reductions are reported in the literature. Inspection of these sources offers no rationale as to why a specific cosolvent in a given system was selected over another.¹⁰ Cosolvent certainly affects the redox potential of SmI_2 and, therefore, is important in determining the rates and energetics of electron transfer from SmI_2 to a reducible species (if it occurs through an outer-sphere process). It seems reasonable to expect that the structure of the cosolvent, its steric bulk, and its basicity are factors that will affect the oxidation potential of the SmI_2 -cosolvent reducing reagent. Electrochemical techniques provide a convenient method for probing the energetics of single electron transfer (SET) from SmI_2 and SmI_2 -cosolvent complexes. Knowledge of the free energies of

electron transfer (expressed through the redox potentials) are essential because they address the driving forces for electron transfer in reductions mediated by SmI₂ and allow direct examination of the effects of cosolvent and its concentration on the free energies of SET.

Table 1 presents the results of the linear sweep voltammetric analysis of SmI₂ solutions containing various cosolvents. Cosolvents and additives containing basic oxygen or nitrogen should coordinate to SmI₂. The effect of cosolvent concentration on the peak potential for oxidation (E_{ox}) of SmI₂ was determined by plotting the change in the E_{ox} of SmI₂ vs. cosolvent concentration. The resulting curves plateau at the point where further addition of cosolvent has no effect on the E_{ox} of SmI₂. The change in the reducing power of SmI₂ is dependent on the nature and concentration of the cosolvent.

Table 1
Oxidation Potentials of SmI₂ and SmI₂-Cosolvent Mixtures in THF.

Reducing species	Peak Potential for Oxidation (E _{ox}) (V)	Additive ratio ^a [cosolvent]/[SmI ₂]	Additive Concentration ^b mM	ΔE, V (kcal/mol) ^c
SmI ₂	-1.33			
SmI ₂ - TMP	-1.80	120	600	0.47 (10.8)
SmI ₂ - DBU	-1.84	60	300	0.51 (11.8)
SmI ₂ - PMP	-1.90	12	60	0.57 (13.1)
SmI ₂ - TMU	-2.04	60	300	0.71 (16.4)
SmI ₂ - HMPA	-2.05	4	20	0.72 (16.6)
SmI ₂ - NMP	-2.10	60	300	0.77 (17.8)
SmI ₂ - DMPU	-2.21	30	150	0.88 (20.3)

All potentials were determined vs. a Ag/AgNO₃ electrode in THF employing linear sweep voltammetry at a scan rate of 100 mV/s. The working electrode was glassy carbon. Tetrabutylammonium hexafluorophosphate at a concentration of 0.1 M was employed as an electrolyte. The concentration of SmI₂ is 5mM in a 10 mL electrochemical cell. The reproducibility of all of the oxidation potentials is ±10 mV. ^a based on the minimum equivalents of cosolvent necessary to maximize the oxidation potential. ^bMolarity of additive in THF. ^cΔE represents the difference between the peak potential for oxidation of SmI₂ and SmI₂-cosolvent species.

The result of our previous work on the effect of HMPA on the reducing power of SmI₂ reveals that it takes four equivalents of HMPA for the oxidation potential to reach a plateau, suggesting coordination of four HMPA ligands to samarium.¹¹ These results are consistent with two recent studies. Curran found that four equivalents of HMPA were necessary to maximize the reduction of primary radicals¹² and Hou successfully isolated and structurally characterized the complex SmI₂-(HMPA)₄.¹³ Trimethyl phosphate (TMP) and pentamethylphosphoramidate (PMP) [((CH₃)₂N)₂(CH₃O)P(O)], were examined and compared with HMPA. The behaviors of TMP and PMP are different than that of HMPA in a number of respects. More than four equivalents of these additives are necessary to fully maximize the oxidation potential of SmI₂. The increase in E_{ox} occurs gradually with each successive addition of TMP, reaching a plateau of -1.80 V at 120 equivalents. The increase in E_{ox} of SmI₂ occurs more dramatically with each successive addition of PMP, reaching a plateau of -1.90 V at 12 equivalents of the additive. It is unlikely that more than six equivalents of these additives can actually ligate to SmI₂.¹⁴ The reduced basicity of the phosphoryl oxygen of PMP and TMP compared to that

of HMPA is probably responsible for the different behavior of the related cosolvents. A larger concentration of the less basic cosolvents is necessary to push the equilibrium to the fully ligated SmI_2 reducing species. Steric bulk plays some role in the ability of a cosolvent to ligate to SmI_2 . We discovered that triphenylphosphite had no effect on the oxidation potential of SmI_2 , even at very high concentrations.

Additives containing urea and amide functionalities have been reported to enhance the rate of SmI_2 -mediated reductions and offer a safer alternative to HMPA.^{1d,6,7} N-methyl-2-pyrrolidinone (NMP) was found to increase the E_{ox} of SmI_2 by 0.77V. The structurally similar ureas DMPU and TMU were examined and were found to exhibit different behavior. The reducing species formed between DMPU and SmI_2 began to precipitate once more than 30 equivalents of the cosolvent was added while the reagent formed from the addition of TMU to SmI_2 remained soluble even at high concentrations of cosolvent. The SmI_2 -TMU reducing species was determined to have an E_{ox} of -1.99 V at 30 equivalents of cosolvent while the SmI_2 -DMPU complex displayed an E_{ox} of -2.21 V at the same cosolvent concentration. The E_{ox} of SmI_2 -TMU reached a plateau of -2.04V at 60 equivalents. The acyclic TMU may be a better choice of cosolvent for SmI_2 reductions and reductive couplings because of its solubility in THF.

Although additives to SmI_2 reductions generally contain basic oxygen, cosolvents containing basic nitrogen should also increase the reducing power of SmI_2 . We employed 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to determine the impact of nitrogen ligands on the oxidation potential of SmI_2 . Cabri and coworkers found that DBU was an effective cosolvent for enhancing the rates of cyclizations mediated by SmI_2 .¹⁵ They also noted that only two equivalents of DBU were necessary for their reductions. We discovered that two equivalents of this additive had only a small influence on the reducing power of SmI_2 . In fact, 60 equivalents of DBU were needed to reach a plateau in the E_{ox} of SmI_2 . One problem we have found in all of these studies is that even a small amount of water can have an effect on the measured oxidation potential (reducing power) of SmI_2 . For instance, the oxidation potential of the SmI_2 -TMP cosolvent mixture is lowered to -1.70 V in the presence of trace amounts of water. Curran recently determined that water can accelerate certain types of SmI_2 -mediated reductions.^{6a} We determined the effect of water on the E_{ox} of SmI_2 and found that 55 equivalents of water increases the oxidation potential of SmI_2 to -1.74 V. Water may compete with cosolvent for coordination to SmI_2 and may influence the outcome of reactions not only by altering the oxidation potential of SmI_2 , but also by changing the steric bulk of the SmI_2 -cosolvent reducing species.

The voltammetric analysis of the cosolvents and additives shows that different ligands have different affinities for SmI_2 in THF. HMPA appears to have the highest affinity for SmI_2 followed by PMP, DMPU, TMU, NMP, DBU, and finally TMP. Examination of crystal structures obtained by Hou and coworkers on the $\text{SmI}_2(\text{HMPA})_4$ ¹² and $\text{Sm}(\text{HMPA})_6\text{I}_2$ ¹⁶ complexes shows that the $\text{Sm}(\text{II})$ -HMPA reducing reagents are very sterically crowded. If the fully ligated $\text{Sm}(\text{II})$ reductant is important in the selectivity of $\text{Sm}(\text{II})$ mediated bond forming reactions,¹⁶ higher concentrations of cosolvents and additives with low affinities for divalent Sm will be necessary to produce a crowded reductant. If a sterically congested complex is formed, it is improbable that reducible halides and carbonyls will be able to enter the inner sphere of the crowded $\text{Sm}(\text{II})$ reductant (at least in the initial electron transfer step). Also, since the ketones, aldehydes, and halides that are reduced in these reactions are less basic than most of the common cosolvents, it is unlikely that they will displace the more basic ligands. Therefore we hypothesize that basic cosolvents like HMPA will produce $\text{Sm}(\text{II})$ reductants that carry out reductive transformation via outer-sphere electron transfer. We are currently examining this supposition.

The initial results contained in this communication provide strong evidence that it is possible to "fine tune" the reducing power of SmI_2 through both changes in the cosolvent structure and its concentration. The influence of cosolvent on the rates of SmI_2 mediated reactions is currently being examined in our laboratory. We expect that basic, bulky cosolvents will produce sterically crowded reducing reagents that carry out reductions via an outer-sphere electron transfer. The influence of different cosolvents and their concentrations on the selectivities of SmI_2 -mediated coupling reactions and reductions and the relationship to the energetics of SET will be presented in a forthcoming full paper.

Acknowledgment: RAF is grateful to the donors of the Petroleum Research Fund, administered by the ACS, (29492-G1) for support of this research. JRF would like to thank the Proctor & Gamble Company and the University of Toledo Honors Program for undergraduate research funding. We would like to thank Dr. Rebecca Miller and Mr. Andrei Caracoti for their useful comments on the manuscript.

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