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Aggregation state and reducing power of the samarium diiodide–DMPU complex in acetonitrile

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Abstract

The aggregation state of SmI_2 and the reducing power of SmI_2 and its DMPU complex were investigated employing vapor pressure osmometry (VPO) and cyclic voltammetry (CV), respectively. The aggregation number for SmI_2 in acetonitrile was found to be 1.03 ± 0.07 over the entire concentration range studied indicating that SmI_2 is monomeric. The CV study showed that DMPU enhances the reducing power of SmI_2 in acetonitrile but that the resulting complex is not as powerful as the SmI_2–HMPA complex in THF. The CV study also showed that solvent could alter the reducing power of SmI_2. © 2000 Elsevier Science Ltd. All rights reserved.

Samarium diiodide, SmI_2 is one of the most versatile reducing reagents utilized by organic chemists because it can be used to reduce and couple a wide range of functional groups.[1] It is clear that while SmI_2 is an important reagent in the arsenal of synthetic chemists, very little is known about its mechanism of action. Cosolvents such as HMPA play a crucial role in many SmI_2-mediated reductions in THF.[2] We have extensively studied the aggregation state of SmI_2 in THF and the thermodynamics of complex formation with HMPA.[3,4] Our work clearly shows that SmI_2 exists as a solvated monomer in THF.

Although most chemistry employing SmI_2 in synthesis is carried out in THF, it can be used in other solvents as well. Recently, the preparation and reactivity of SmI_2 in tetrahydropyran (THP) was described.[5] Benefits of this medium include the absence of by-products due to ring opening of THF and the possibility of carrying out reductive coupling of acid chlorides with aldehydes and ketones. Namy and Kagan recently reported the preparation and reactions of SmI_2 in nitriles.[6] They found that while reactions were slower in pivalonitrile than in THF, the selectivities and yields of reductive coupling reactions were better. In a separate study, Ruder found that the SmI_2-mediated reductive coupling of acid halides with ketones produced high yields of α-hydroxyketones when carried out in acetonitrile.[7] Curran studied the effects of

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HMPA, DMPU, and water on SmI_2 reductions in THF and acetonitrile and found that while DMPU is not an effective additive in THF, it is quite effective in acetonitrile.[8]

Although the combination of HMPA with SmI_2 in THF provides a powerful reductant, other effective cosolvents and additives can provide an alternative to the toxic HMPA. Another issue deals with solvation of the Sm reductant. Solvation of Sm(II) likely affects the reducing power and aggregation state of the reductant, so solvents other than THF may either alter access to the metal center by reducible substrates or provide a differential perturbation to the electron donating orbital of the reductant. The net result in any of these scenarios is a change in the reactivity of the Sm reductant. In order to examine the suppositions above, we studied the aggregation state of SmI_2 in acetonitrile and examined the influence of DMPU on the reducing power of the resulting Sm(II) complex.

Solutions of SmI_2 in acetonitrile were prepared by the method of Curran and coworkers.[9] It should be noted that exhaustively dried acetonitrile is necessary for successful preparation of SmI_2. Vapor pressure osmometry (VPO) was used to determine if SmI_2 is a solvated monomer in acetonitrile or if it is a higher order aggregate. The aggregation numbers for SmI_2 in acetonitrile at four different concentrations are contained in Table 1. The anticipated precision for these measurements is approximately ±10%. The average value for the aggregation number of SmI_2 at four different concentrations is 1.03±0.07. The data shown in Table 1 clearly indicate that SmI_2 is monomeric in acetonitrile over the concentration range examined in this study. The higher end of the concentration range studied in the VPO experiments is at the solubility limit of SmI_2 in acetonitrile so it is likely that SmI_2 is always monomeric under normal reaction conditions. The VPO experiments also indicate that any change in the reactivity of SmI_2 when used in THF versus acetonitrile is not due to reductant aggregation.

Table 1
Concentration and aggregation numbers (VPO) of SmI_2 in acetonitrile

Entry	Standardized concentration (mmolal)	VPO Molality	Aggregation number[a]
1	80.6	84.2±0.4	0.96±0.01
2	40.3	41.3±0.7	0.98±0.02
3	32.2	28.9±0.7	1.11±0.03
4	19.3	18.2±0.5	1.06±0.03
			Average value = 1.03±0.07

[a] ±Values are reported at the 95% confidence level.

Next we examined the effect of DMPU on the redox potential of SmI_2 in acetonitrile. The relationship between cosolvent concentration and the redox potential of SmI_2 was examined by adding successive 1 equivalent amounts of DMPU and recording a cyclic voltammogram for each addition. During the addition of DMPU, the potential continued to shift to more negative values until 10 equivalents of the cosolvent was added. Further addition of DMPU showed no effect on the redox potential. It is unlikely that more than 6 equivalents of DMPU can actually ligate to SmI_2 due to obvious steric constraints.[10] Earlier work in our laboratory showed that a larger concentration of cosolvents that are less basic than HMPA are necessary to push the equilibrium to the fully ligated SmI_2 reducing species.[11]

Fig. 1 contains the cyclic voltammograms of SmI_2 and SmI_2 containing 10 equivalents of DMPU. Both of the voltammograms shown in Fig. 1 are quasireversible so we employed the model recently described by Skrydstrup for the SmI_2^+–SmI_2 redox couple to estimate the standard potentials.[12]

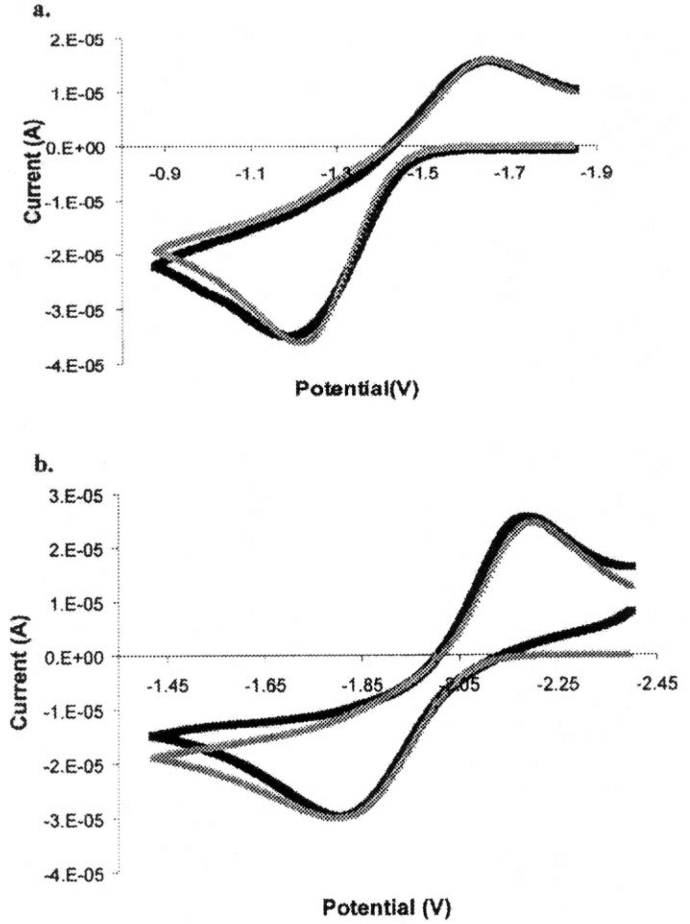

Figure 1. (a) Cyclic voltammogram of SmI_2 recorded in acetonitrile containing 0.5 M tetrabutylammonium hexafluorophosphate at a glassy carbon electrode (diameter = 1 mm) using a sweep rate of 100 mV s^{-1}. (b) Cyclic voltammogram of SmI_2–DMPU recorded under the same conditions. The gray curves represent the simulated voltammograms.

Digital simulation of both voltammograms revealed that the standard potential (versus $Ag/AgNO_3$) for SmI_2 in acetonitrile is −1.44±0.05 V while the standard potential for the SmI_2–DMPU complex is −2.08±0.06 V. The addition of DMPU increases the reducing power by 0.64 V (14.8 kcal/mol). It is useful to compare the standard potentials of SmI_2 and SmI_2–DMPU with the redox potentials for SmI_2 and SmI_2–HMPA in THF. The standard redox potentials (versus SCE) of SmI_2, its HMPA complex in THF and the values for SmI_2 and SmI_2–DMPU versus SCE are displayed in Table 2. Two main points are apparent. First, the SmI_2–HMPA complex in THF is a better reductant than the SmI_2–DMPU complex in acetonitrile. Second, SmI_2 is a stronger reductant in THF than it is in acetonitrile by 0.14±0.06 V (3.2±1.4 kcal/mol). This finding shows that the change in solvation of the Sm(II) has a modest impact on its reducing power. We have recently shown that standard redox potentials in combination with Marcus theory can be used to predict the mechanism of electron transfer (ET) from SmI_2 to reducible substrates.[13,14] The change in the redox potential of SmI_2 from THF to acetonitrile suggests that the rate and possibly the mechanism of ET may be solvent dependent. Studies exploring this possibility are in progress and will be reported in due course.

Table 2
Standard potentials for SmI_2 complexes

Entry	Reductant	Standard potential, V (versus SCE)
1	SmI_2 (THF)[a]	-0.98 ± 0.04
2	SmI_2–HMPA (THF)[a]	-1.75 ± 0.06
3	SmI_2 (acetonitrile)	-0.84 ± 0.05[b]
4	SmI_2–DMPU (acetonitrile)	-1.48 ± 0.06[b]

[a] Reported in Ref. 11.

[b] The difference between the SCE and Ag/$AgNO_3$ is 0.6 V.

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