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Rapid SmI_2-Mediated Reductions of Alkyl Halides and Electrochemical Properties of SmI_2/H_2O/Amine

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Mixtures of SmI_2/H_2O/amine have been found to reduce alkyl halides more efficiently than SmI_2/HMPA/alcohol mixtures at room temperature. Alkyl and aryl iodides were quantitatively reduced in <1 min and alkyl bromides in 10 min, while alkyl and aryl chlorides required more than 5 h for completion. Determination of the reaction order of Et_3N in the reduction of 1-chlorodecane showed that the reaction order is one. Water was shown not to participate in the rate-determining step of this reduction. There was a significant change of the UV−vis spectrum and color of SmI_2 upon addition of either PMDTA or water, while no effect was observed with the addition of Et_3N or TMEDA. Although the combination of SmI_2, water, and amines produces a very efficient reducing system, cyclic voltammetric experiments showed that the redox potential is nearly identical with that of SmI_2 alone. These results are consistent with precipitation providing the driving force for reduction. Taken together, the results of these experiments show that the combination of SmI_2/H_2O/amine provides a fundamentally novel and useful approach to enhance the reactivity of SmI_2.

Introduction

Samarium(II) diiodide was introduced as a reducing agent by Kagan and co-workers in 1980.[1] Since then a number of SmI_2-based reactions including reductions,[2] reductive couplings,[3] and sequenced reactions[4]have been developed, and new applications for this selective single electron transfer reagent are steadily being discovered.

Samarium diiodide is a rather mild reducing agent and strongly coordinating cosolvents are necessary to enhance the rate of some SmI_2-mediated reactions. In particular, HMPA has been found to drastically increase both the reactivity and selectivity of many reactions.[5] While other cosolvents have been used in SmI_2-based reactions none have the general utility of HMPA.[6,7] Although countless reactions require SmI_2−HMPA for success, the major negative aspect of this reducing system is the high carcinogenicity of HMPA.

Recently two of us (A.D. and G.H.) have discovered that the combination of SmI_2/amine/water is superior to SmI_2−HMPA in some reactions.[8,9] During our study of SmI_2/H_2O/amine mixtures we have previously reported that ketones, imines, and α,*β*-unsaturated esters are reduced instantaneously, i.e. completed in less than 10 s.[9] Furthermore, it has been shown that the combination of amine and water has a remarkably strong effect on the reactivity of SmI_2 for the reduction of olefins as well.[8b] In particular, alkyl chlorides are known to be somewhat more difficult to reduce compared to other functional groups, e.g. ketones, imines, and α,*β*-unsaturated esters,[1,10] and we wanted to examine the utility of this protocol in the reduction of this more recalcitrant case.

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TABLE 1. Completion Times in the Reduction of Alkyl Halides by Excess SmI_2/H_2O/Amine[a]

substrate	product	Et_3N	TMEDA	PMDTA
1-chlorodecane	*n*-decane	14 h	24 h	10 h
1-bromodecane	*n*-decane	5 min	15 min	2 min
1-iododecane	*n*-decane	<1 min	<1 min	<1 min
chlorocyclohexane	cyclohexane	6 h	12 h	4 h
chlorobenzene[b]	benzene[b]	5 h	10 h	2 h
bromobenzene	benzene	40 min	90 min	20 min
iodobenzene	benzene	<1 min	<1 min	<1 min
benzyl chloride	toluene	<1 min	<1 min	<1 min

[a] Approximate completion times determined by GC for yields above 95% by excess SmI_2 (7 equiv), H_2O (35 equiv), and amine (28 equiv) at 20.0 °C (pseudo-first-order rate conditions). [b] Chlorobenzene did not go to completion without a large excess of SmI_2, the completion time thus represents a 50% yield.

Herein we present our recent results in SmI_2-mediated reductions of alkyl halides using SmI_2/H_2O/amine mixtures, including completion times for several alkyl halides and initial rate measurements. Electrochemical and spectroscopic experiments were utilized to investigate the properties of SmI_2/H_2O/amine combinations. Three different amines, triethylamine (Et_3N), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylene triamine (PMDTA), have been used together with SmI_2 and water in these studies. The results of this study show that while the mechanism of reduction of alkyl halide by SmI_2/H_2O/amine is different than the reduction of ketones, olefins, and imines by the same procedure, the main driving force for the reaction remains precipitation of Sm^{3+}. The protocol described in this paper provides a fundamentally novel approach for enhancing the reactivity of SmI_2.

Results

Reduction of Alkyl Halides by SmI_2/Water/Amine. The mixtures of SmI_2/H_2O/amine in THF were employed in the reduction of various alkyl halides. The results of the reductions with either of the amines Et_3N, TMEDA, and PMDTA are summarized in Table 1. The mixture of SmI_2/H_2O/amine in THF is also effective in the reduction of halides; however, these reactions are not as fast as the reduction of ketones. In analogy with other studies we find that the iodides are reduced more easily than the bromides and chlorides, in that order.[1,2c,5c] The aliphatic halides are reduced faster than their aromatic analogues, e.g. 1-bromodecane is completely reduced in 5 min while bromobenzene requires 40 min with SmI_2/water/Et_3N. Secondary halides react faster than primary alkyl halides (chlorocyclohexane is reduced in 6 h while 1-chlorodecane requires approximately 14 h with SmI_2/water/Et_3N). It was also noted that the use of excess amine further enhanced these reductions, thus we used approximately 4 equiv of R_3N per SmI_2 to attain the completion times listed in Table 1.

Introducing benzyl chloride into a samarium diiodide solution in THF typically results in the coupled product bibenzyl in about 1.5 h.[11] Attempts to avoid this dimerization and instead produce toluene by means of MeOH addition provide a mixture of both products (Figure 1).

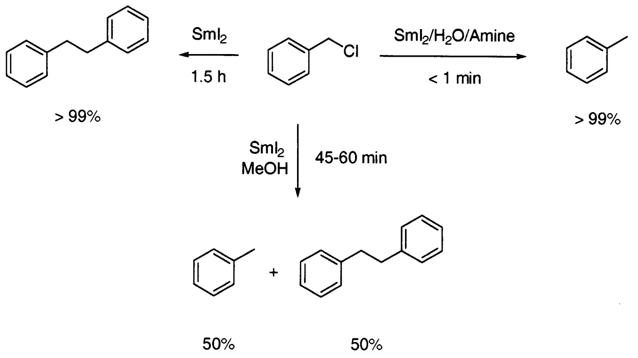

FIGURE 1. Alternative reaction pathways of benzyl chloride with SmI_2.

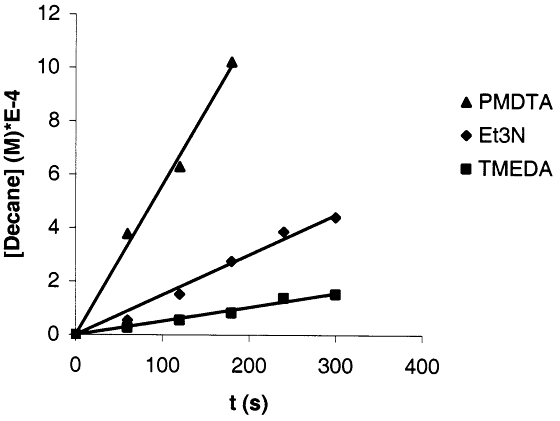

FIGURE 2. Rate comparison for 1-chlorodecane (1 equiv) by SmI_2 (7 equiv), R_3N (14 equiv), and H_2O (17.5 equiv).

However, utilizing SmI_2/H_2O/amine mixtures in the reduction of benzyl chloride results exclusively in the dehalogenated product toluene in <1 min.

Initial Rate Measurements. Reaction rates were measured by monitoring the appearance of *n*-decane and disappearance of 1-chlorodecane in quenched aliquots by GC. The initial rates were obtained by following each reaction from approximately 0.1% to between 1% and 6% completion. There are differences in the rate of reduction with the three amines (Et_3N, TMEDA, and PMDTA) and it appears that PMDTA is superior to the other two amines. TMEDA seems to mediate the reduction with an unexpected slower rate compared to that of triethylamine (Figure 2).

The increase in rate is linear to the increase in concentration of triethylamine and no saturation is observed even at 16 equiv of amine/SmI_2 (Figure 3). Varying the triethylamine concentration from 0.1 to 1.3 M the reaction order (equal to the slope) of triethylamine was found to be ca. 1 by plotting log[rate] vs log[triethylamine] (Figure 4). By varying the water concentration we also found that the initial rate of reduction of 1-chlorodecane is independent of $[H_2O]$.

Primary Kinetic Isotope Effect. The primary kinetic isotope effect (PKIE) in the reduction of 1-bromodecane and 1-chlorodecane with the mixture of SmI_2/water/amine was also studied. The rates of reduction with H_2O and D_2O were identical, i.e., $k_H/k_D = 1$, indicating that the proton transfer is not involved in the rate-determining step. As a consequence, no PKIE was

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[11] Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chem.* **1977**, *1*, 5−7.

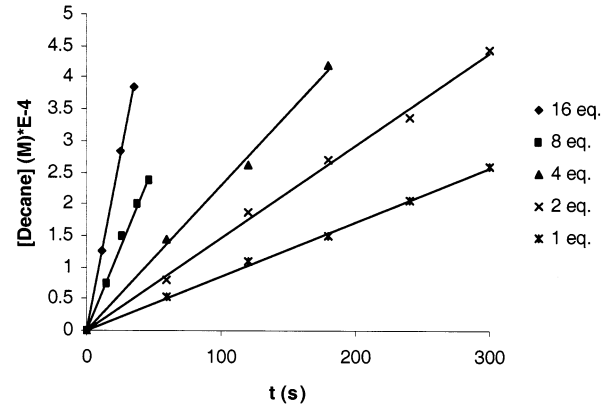

FIGURE 3. Reduction of 1-chlorodecane (1 equiv) by SmI_2 (7 equiv), H_2O (35 equiv), and varying amounts of Et_3N.

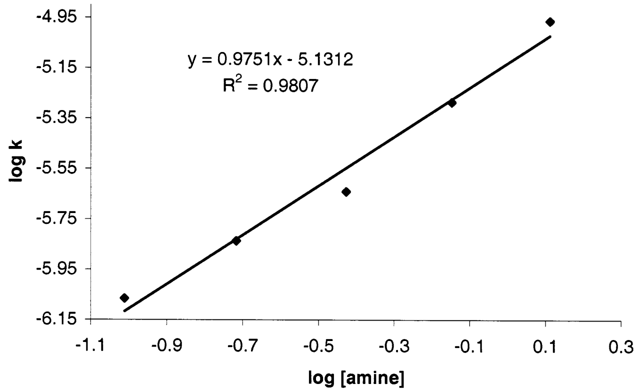

FIGURE 4. Determination of the reaction order of Et_3N in the reduction of 1-chlorodecane.

obtained in the absence of amines. However, the rate of the reduction was considerably lowered for the SmI_2-mediated reduction induced by water in comparison with a mixture of PMDTA and water.

Titrations. Previously we reported that 6 equiv of water and 4 equiv of R_3N are needed to obtain the instantaneous reduction of ketones (eq 1).[8a] Carrying out

$$R_2C{=}O + 2SmI_2 + 6H_2O + 4R_3N \rightarrow R_2CHOH + 2Sm(OH)_3 + 4R_3N{\cdot}HI \quad (1)$$

the same analysis on alkyl iodides, i.e., adding the amine and water, respectively, in portions to a mixture of SmI_2, water, and the alkyl iodide, results in the reaction shown in eq 2. The titrations indicated that one additional equivalent of R_3N was needed, compared to ketone reductions, to achieve the fast quantitative reduction of the alkyl iodide. This additional amine is required for the extra halide X that is generated when RX is reduced to RH.

$$R{-}X + 2SmI_2 + 6H_2O + 5R_3N \rightarrow R{-}H + 2Sm(OH)_3 + 4R_3N{\cdot}HI + R_3N{\cdot}HX \quad (2)$$

$$X = Cl, Br, I; R = alkyl, aryl$$

This supports the hypothesis that these salts are precipitated during SmI_2/H_2O/amine mediated reactions.

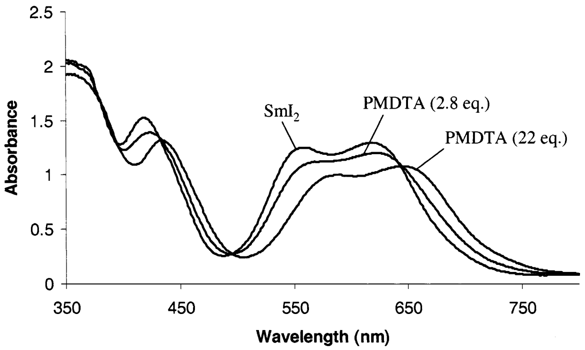

FIGURE 5. UV−vis of PMDTA/SmI_2 mixtures compared to SmI_2 in THF.

UV−Vis Studies of SmI_2 Complexes. To achieve additional information of the SmI_2/amine complexes a series of UV−vis experiments were conducted. Previously UV−vis spectra have been reported for SmI_2 and SmI_2/HMPA complexes.[6a,12] Samarium diiodide in THF has a characteristic appearance in the UV−vis absorbing wavelengths at 418, 557, and 618 nm, respectively. Additions of triethylamine in increasing portions had no effect on the UV−vis spectrum. The addition of TMEDA (1−32 equiv) gave a small, but relatively insignificant, change of the absorbances to 420, 562, and 622 nm, respectively. However, addition of PMDTA (1−22 equiv) resulted in a large shift of the wavelengths of SmI_2 to 435, 588, and 650 nm. The presence of the isosbestic point at 493 nm shows that only two absorbing species are present in solution.[13]

The results indicate that neither triethylamine nor TMEDA coordinate to any significant amount to samarium diiodide. However, with the addition of PMDTA there is an observed shift of approximately 30 nm indicative of coordination (Figure 5). The SmI_2/PMDTA complex is also identified by a characteristic green color.

Next a number of experiments were performed to determine the affinity order of different additives (PMDTA, TMEDA, DMPU, and water). The additives were added to SmI_2 in dissimilar order and compared with use of UV−vis. The strongest bonding additive of the investigated additives was water, which coordinates to SmI_2 regardless of the order of addition of the different additives. These experiments indicate the following order of affinity: TMEDA < PMDTA < DMPU < H_2O. The UV−vis spectra of SmI_2 containing water or DMPU are presented in Figures 6 and 7.

The characteristic blue color of SmI_2 turned deep red in the presence of water, while addition of PMDTA resulted in a green shade and DMPU or HMPA in a purple shade, respectively. The characteristic ligand-dependent color changes make differentiation of the preferred coordinating ligand to SmI_2 easily observable, since the ligand with the highest affinity will also determine the color of the complex (Table 2). There is no combination of these additives that gives rise to a new

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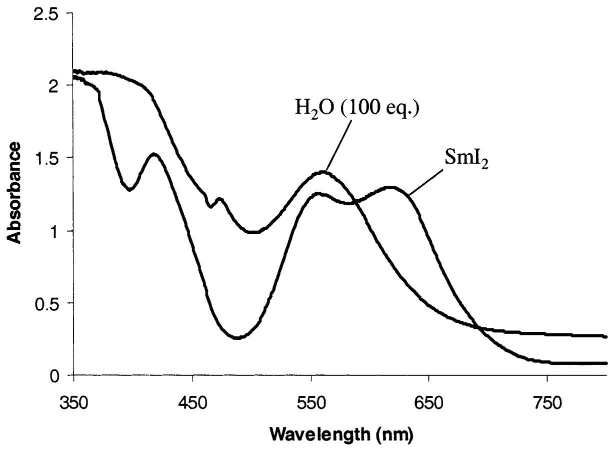


FIGURE 6. UV−vis of the H_2O/SmI_2 complex compared to SmI_2 in THF.

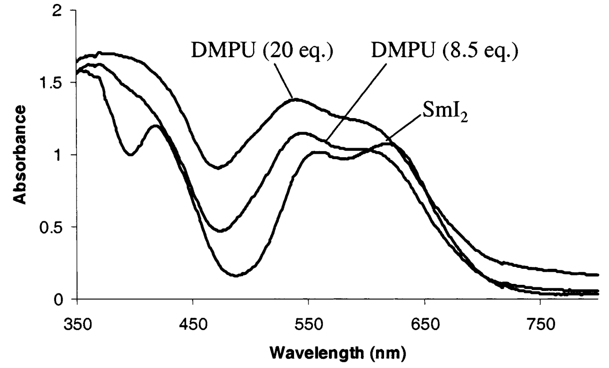


FIGURE 7. UV−vis of DMPU/SmI_2 mixtures compared to SmI_2 in THF.

TABLE 2. UV−Vis Properties of SmI_2 Complexes.

mixture in THF	absorbed wavelengths	color
SmI_2	418, 557, 618	blue
SmI_2/H_2O	474, 557	red
SmI_2/PMDTA		

UV spectrum indicating that there are no mixed solvated SmI_2 species.

Cyclic Voltammetry Investigation. Cyclic voltammetry was utilized to estimate the redox potential of SmI_2−PMDTA allowing comparison to potentials known for SmI_2[5a,b,6e] and other Sm(II) complexes. Figure 8 shows the CV data for SmI_2 and SmI_2 containing PMDTA. Interestingly, there is little change in the potential (as determined from the oxidation and reduction peaks from the voltammogram). Careful inspection of the voltammograms shows that the oxidation peak shifts to a more positive potential while the position of the reduction peak is the same within experimental error. The potential for SmI_2 was estimated to be -1.55 ± 0.05 V vs $Ag/AgNO_3$, while the potential of SmI_2-containing PMDTA was estimated to be -1.4 ± 0.1 V vs $Ag/AgNO_3$.

Furthermore, as larger amounts of PMDTA are added to the SmI_2, there is considerable distortion in the shape of the anodic and cathodic peaks. Since the changes in the cathodic and anodic peaks were relatively small, the voltammograms in Figures 8 and 9 were recorded at different concentrations for clarity.

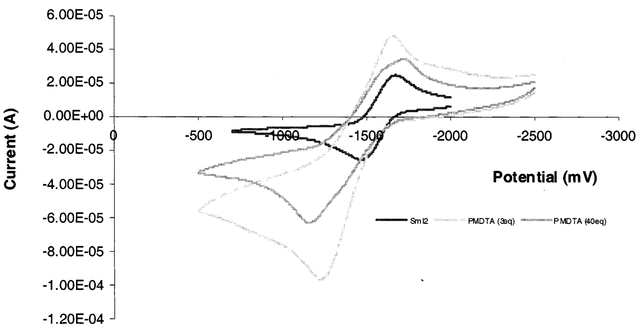


FIGURE 8. Cyclic voltammograms for SmI_2, SmI_2 with PMDTA (3 equiv), and SmI_2 with PMDTA (40 equiv), respectively.

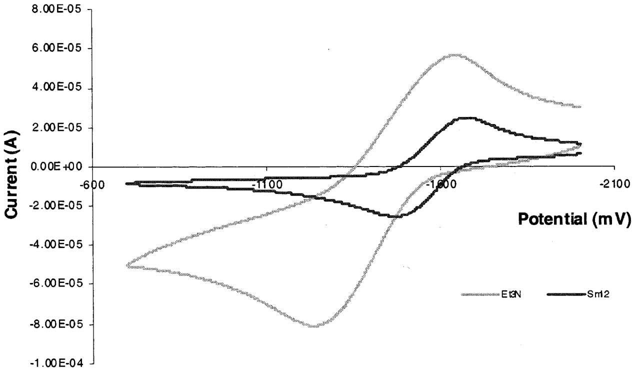


FIGURE 9. Cyclic voltammograms for SmI_2, and SmI_2 containing 3 equiv of triethylamine.

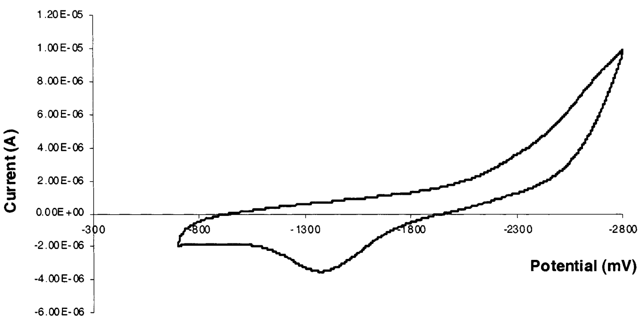
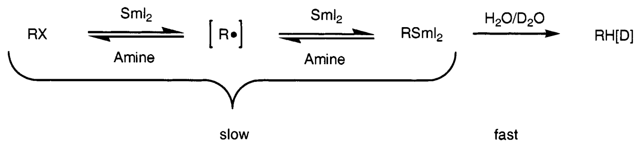


FIGURE 10. Cyclic voltammograms for SmI_2/H_2O/triethylamine.

Figure 9 includes the CV of SmI_2 and SmI_2-containing triethylamine. In a manner similar to the addition of PMDTA, the oxidation peak shifts slightly to a more positive value upon addition of triethylamine. Next, we added 2 equiv of triethylamine and 2.5 equiv of water to a solution of SmI_2. This ratio of SmI_2/amine/H_2O was initially reported to be sufficient in the reduction of ketones and imines.[9] Changing the ratio of SmI_2/amine/H_2O to the present conditions had no effect on the potential or behavior of the system. The CV is shown in Figure 10.

While the oxidation peak shows little difference from the SmI_2−amine complex, the reduction peak disappears. In fact, if we carried out a series of successive cyclic voltammetric experiments on the same sample, the solution slowly decolorized and the oxidation peak disappeared as well. During these experiments, precipitation

SCHEME 1. Reduction of Alkyl Halides by SmI_2/Amine/H_2O



was evident in the bottom of the electrochemical cell. We made numerous attempts to examine the combination of SmI_2/PMDTA/H_2O but could not obtain reproducible results.

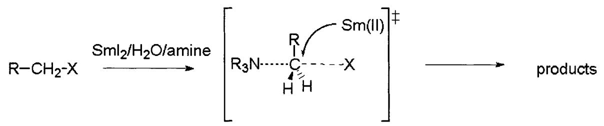
Discussion

The initial rate studies clearly showed that the rate of reduction of alkyl halides was independent of water concentration. Further studies with D_2O showed no kinetic isotope effect either in the presence or in the absence of amines. This finding is in contrast to the reduction of ketones, which shows a PKIE.[9,14] Even though these experiments show that water is not involved in the rate-determining step of the reaction, the presence of 3 equiv of water per SmI_2 is crucial for the completion of the reaction.

The linear correlation of log[rate] vs log[Et_3N] with the gradient equal to 1.0 shows that the amine is intimately related to the rate-determining step of the reduction. These results suggest that reduction of alkyl halides to a radical or the subsequent reduction to an organosamarium is the rate-determining step for the SmI_2/H_2O/amine mediated reduction of alkyl halides.

The UV–vis studies of SmI_2/amine mixtures show that only the tridentate amine PMDTA coordinates to samarium. The presence of the isosbestic point at 493 nm is good evidence that there are only two primary absorbing species present in solution, most likely SmI_2/THF and SmI_2/PMDTA. There is no change in the UV–vis spectra of SmI_2 upon addition of either Et_3N or TMEDA. Clearly the bulk solvent THF is a stronger coordinating ligand for samarium diiodide than Et_3N or TMEDA. It is, however, important to remember that the UV studies are performed on the initial state complexes, i.e., the amine (Et_3N) may coordinate to the samarium in the transition state even if it does not coordinate in the initial state. For instance, it has been shown that TMEDA is involved in the rate-determining step of certain lithiation reactions performed in THF even though TMEDA is clearly not coordinated to the lithium reagent in the initial state.[15] We propose that the rate-determining step of the SmI_2/H_2O/amine mediated reduction of alkyl halides is the formation of organosamarium species. This insertion reaction may be mediated by one coordinated molecule of amine in the transition state. If this supposition is correct, H_2O is consumed after this rate-limiting step.

SCHEME 2. Nucleophile-Assisted Displacement of Halides



Another potential mechanism that describes the involvement of amine could involve assistance in displacing the halide from the organic substrate (Scheme 2). Amines can certainly act as nucleophiles and it is possible that the amine may not coordinate to SmI_2 in the transition state but could assist the displacement of the halide in the transition state. Further studies will be required to distinguish these two potential mechanistic scenarios.

The UV studies also showed that water is readily coordinated to samarium diiodide and that there is a substantial change in the UV spectra. The spectra of SmI_2/H_2O and SmI_2/DMPU are in fact similar. While the role of water is important to drive the formation of the Sm^{3+}, it is possible that water also influences the redox potential of SmI_2, making it a better reductant.[16] Conversely, the CV data indicate that the influence of the amine/H_2O combination has a relatively small influence on the redox potential of SmI_2.

The effects of the amines are very intriguing. The only amine that affects the UV spectra is PMDTA, and the addition of PMDTA to SmI_2 results in a substantial bathochromic shift. By adding mixtures of additives we could also establish an affinity order according to the following: TMEDA < PMDTA < DMPU < H_2O. Thus H_2O is the best ligand for SmI_2 and it competes well with the other ligands when coordinating to SmI_2. A potential way to further enhance the rates of aliphatic alkyl halides may be a combination of this method, i.e., SmI_2/H_2O/amine, with the addition of a cosolvent, e.g. DMPU or DBU.

Conclusion

The experiments described in this paper show that the combination of SmI_2/H_2O/amine has a profound impact on the rate of reduction of alkyl halides. The mechanistic studies show that 1 equiv of amine is involved in the rate-determining step of the reaction and while the presence of water is necessary for reduction of alkyl halides, it comes in to play after the rate-limiting step of the reaction. Regardless of the discreet mechanistic details of the reduction of alkyl halides, the combination of SmI_2/H_2O/amine profoundly accelerates the reduction of alkyl and aryl halides, ketones, imines, and other functional groups. Further mechanistic studies of this powerful combination and its utility in other reductions and reductive coupling reactions will be presented in due course.

Experimental Section

General. THF was distilled from sodium and benzophenone under nitrogen atmosphere. The amines were distilled under nitrogen atmosphere and stored over molecular sieves. SmI_2, additives, and solvents were stored under nitrogen atmosphere in a glovebox containing typically <1 ppm H_2O and O_2, respectively.

Reductions of Alkyl Halides. In a standard initial rate measurement, SmI_2 in THF (0.1 M, 7 equiv) was added to a dry Schlenk tube, fitted with a septum and containing a

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magnetic stirrer bar, inside a glovebox with nitrogen atmosphere. The amine, i.e., Et_3N (28 equiv), TMEDA (14 equiv), or PMDTA (9.5 equiv), and the alkyl halide (1 equiv) were added at 20.0 °C. The proton donor, i.e., H_2O (35 equiv), was added dropwise with a gastight syringe. Small portions of the mixture (100 μL) were removed via a syringe and quenched with I_2 in *n*-hexane (0.1 M, 0.1 mL). To the quenched solutionwere added diethyl ether (1 mL) and HCl (0.12 M, 0.1 mL) to dissolve the inorganic salts and finally $Na_2S_2O_3$ to remove excess iodine. The organic layer was transferred to a vial and the yield of the reaction was analyzed with GC. All products were compared with authentic samples on GC.

Gas Chromatography. The products were separated by using a GC fitted with an achiral stationary phase column ($\phi = 0.25$ mm, length $= 25$ m), using hydrogen as the carrier gas at a flow rate of 2 mL/min. The injector temperature was 225 °C. The column temperature was altered depending on the substrate/products. The detector temperature was 250 °C (FID). The products were identified by using authentic samples.

UV−Vis Measurements. All UV−vis spectra were recorded on a UV−Vis−NIR spectrophotometer connected to a computer. The SmI_2 solutions were diluted to 3.6 mM inside a glovebox in a quartz cuvette equipped with a screwcap fitted with a septum. The path length of the cuvette was 1.00 cm. Successive additions of the additives were made with a gastight syringe through the septum and a new spectrum was recorded after each addition.

Cyclic Voltammetry. The redox potentials of all Sm(II) reagents in THF were independently measured by cyclic voltammetry employing an electrochemical analyzer. The working electrode was a standard glassy carbon electrode. The electrode was cleaned with polishing alumina and then placed in an ultrasonic bath. The auxiliary electrode was a platinum wire and the reference electrode was a saturated Ag/$AgNO_3$ electrode. The scan rate for all studies was 100 mV/s. The electrolyte was either tetrabutylammonium hexafluorophosphate or LiI. The concentration of the Sm(II) species in each experiment was in the range of 0.3 to 0.5 mM. All solutions were prepared in the glovebox and transferred to the electrochemical analyzer for analysis.

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