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Task-Dependent Coordination Levels of SmI2

Sandeepan Maity, Amey Nimkar and Shmaryahu Hoz*

Department of Chemistry, Bar-Ilan University; Ramat Gan-5290002, Israel.

Abstract: Ligation plays a multifaceted role in the chemistry of SmI_2 . Depending on the ligand, two of its major effects are increasing the reduction potential of SmI_2 , and in the case of a ligand which is also a proton donor, it may also enhance the reaction by protonation of the radical anion generated in the preceding step. It turns out that the number of ligand molecules which are needed to maximize the reduction potential of SmI_2 is significantly smaller than the number of ligand molecules needed for maximal enhancement of the protonation rate. In addition to the economical use of the ligand, this information can also be utilized as a diagnostic tool for the reaction mechanism in differentiating between single and multi-step processes. The possible pitfalls in applying this diagnostic tool to PCET and cyclization reactions are discussed.

*E-mail: shoz@biu.ac.il

Introduction

The educated use of additives has made SmI_2 a unique and versatile reducing agent.^{1,2} The role of the additive in SmI_2 -mediated chemistry differs according to its nature. For example, HMPA, one of most common additives in SmI_2 chemistry, is well known for its high affinity to SmI_2 , which leads to formation of a thermodynamically more powerful reductant.³ On the other hand, coordinating proton donors, such as methanol, water, ethylene glycol (EG) etc. enhance the reactivity of SmI_2 by unimolecular protonation of the resultant radical anion within the ion-pair.⁴ This process is much more efficient than the bimolecular protonation by proton donors from the bulk and successfully competes with the back electron transfer from the radical anion to Sm^{3+} and hence 'locks' the reaction.⁵ Some strongly coordinating proton donors such as glycols combine the two features; they raise the reduction potential of SmI_2 and also function as efficient proton donors.^{1g,5a,6}

In the present paper, we employ two additives – EG and *N*-methylethanolamine (NMEA), which are known to provide both thermodynamic (increase in reduction potential) and kinetic (protonation) driving forces to the reactions.^{1g,5a,6a} By following reduction potentials and reaction rates as a function of additive concentration, better insight was obtained into the chemistry of SmI₂.

Results and discussion

The effect of an EG ligand on reactions of SmI_2 was studied by several groups.⁷ It coordinates very well to SmI_2 in THF, as can be seen from its effect on the spectrum of SmI_2 (Figure 1).



Figure 1: The effect of EG on the spectrum of SmI_2 in THF.

In addition, it increases the reduction potential of SmI_2 (Table 1)^{6a} and once bound to the SmI_2 it serves as an efficient protonating agent of the radical anion within the ion pair consisting of the radical anion and $\text{Sm}^{3+.8}$ In Figure 2, the rate constants for the reduction of anthracene are given as function of EG concentration, along with the corresponding reduction potentials of SmI_2 .

Table 1: Cyclic voltammetric data of SmI₂-EG complex^a

[EG]/ M	E1 (V)	E2 (V)	E _{1/2} (V)
0	-1.13	-1.48	-1.3
0.01	-1.35	-1.85	-1.6
0.02	-1.43	-1.89	-1.66
0.03	-1.5	-1.89	-1.69
0.04	-1.52	-1.9	-1.71
0.05	-1.52	-1.94	-1.73
0.1	-1.59	-1.95	-1.77
0.2	-1.6	-1.99	-1.79
0.3	-1.63	-2	-1.81
0.4	-1.64	-2.01	-1.82
0.5	-1.65	-2.01	-1.83

^aE1 and E2 are the oxidative (Sm²⁺ to Sm³⁺) and reductive peak (Sm³⁺ to Sm²⁺) potential respectively. $E_{1/2} = (E_1 + E_2)/2$. E1 values are used for constructing plots with kinetic data.



Figure 2: Reduction potentials (blue) and rate constants (orange) of SmI_2 for anthracene as function of [EG].

It is very noticeable for anthracene that the increase in reaction rate constants with EG concentration lags much behind the increase in reduction potential of SmI_2 . While the rate constants level off at relatively high EG concentrations (>0.5 M), the reduction potential levels off at much lower concentrations (around 0.1 M). The leveling off of the rate constant could originate from a change in the rate determining step, from protonation of the radical anion at low EG concentrations to electron transfer at high EG concentrations. This possibility is ruled out by kinetic H/D isotope effects at 0.05, 0.2 and 0.5 M EG, which were found to be 2.0, 1.9 and 2.0, respectively.^{7a} Hence, protonation is rate determining also at the plateau region. Therefore, a plateau in the rate constants is expected upon completion of the coordination shell of EG molecules around the samarium ion. We have already shown that there is a huge preference for unimolecular protonation by proton donors from the bulk.⁵ Thus, once the coordination sphere is completed, the system attains the maximum number of efficient proton donors, and the rate constant levels off. Additional proton donors will contribute in a bimolecular manner and hence will only marginally affect the protonation rate.

This discrepancy between the concentrations at which the rates of reduction and reduction potentials level off deserves some discussion. As the coordination sphere of the samarium ion is only completed at high EG concentrations (> 0.5 M), it is clear that the coordination of SmI_2 is only partial when the reduction potential levels off (at [EG] ~ 0.1 M). Yet, this partial coordination is sufficient to induce the maximum reduction potential. It is highly likely that this dichotomous

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behavior stems from the significantly different ionic radii of Sm^{2+} (1.22 Å) and Sm^{3+} (0.958 Å),⁹ which translates to a much larger surface area of Sm^{2+} (by more than 50%). The ligand-induced enhancement of the reduction potential of SmI_2 stems from the higher exothermicity of its binding to Sm^{3+} than to the Sm^{2+} .^{6a,10} This shifts the equilibrium toward Sm^{3+} , providing a greater driving force for electron transfer (equation 1).

Substrate + Sml₂ Substrate
$$\cdot$$
 Sml₂ (1)

Due to the smaller ionic radius, Sm^{3+} can accommodate fewer ligand molecules than Sm^{2+} , therefore the reduction potential levels off at a lower coordination level, corresponding to the maximal effective coordination number of Sm^{3+} . On the other hand, efficient protonation depends on the availability of protons within the ion pair, which increases with the number of proton donors coordinated to the SmI_2 .^{2i,5,7a}The reaction rate therefore levels off at significantly higher EG concentrations where full coordination is attained. Even if some EG molecules are shed as the Sm^{2+} transfers an electron and shrinks considerably to the size of Sm^{3+} , these proton donors remain in the reaction cage and are available for a unimolecular protonation of the radical anion.

Based on this understanding, a sterically hindered ligand, which coordinates reasonably well to the larger Sm^{2+} , is expected to coordinate poorly to Sm^{3+} at the concentration in which the maximal reduction potential is attained. Therefore, its effect on the reduction potential will be diminished. Indeed, we find that pinacol (tetramethylethylene glycol) coordinates well to SmI_2 (Figure S4), but hardly raises the reduction potential (from -1.13 to -1.18 V vs. Ag/AgNO₃), compared to EG, which increases the reduction potential of SmI_2 to -1.65 V.

Interestingly, as can be seen in Figure 1, the changes in the spectra of SmI_2 converge around an EG concentration of 0.1 M, similar to the reduction potential.^{6a} This may be explained by considering the cloud of negative charge, which becomes more diffused in the excited state and moves away from the nucleus, mimicking to some extent the smaller radius of Sm^{3+} .¹¹

In order to substantiate the assumption that the slow protonation of the radical anion is responsible for the gap in Figure 2, the same experiment was repeated with benzyl chloride. As can be seen in Figure 3, the rate constants for the reduction of benzyl chloride and the reduction potentials match nicely, both leveling off at an EG concentration of about 0.1 M. This is expected, as benzyl chloride reacts by a mechanism known as a dissociative electron attachment.¹² That is, no intermediate

radical anion is obtained, and the expulsion of the chloride ion takes place concurrently with the electron transfer. Consequently, further addition of EG, beyond the concentration in which the reduction potential, and the electron transfer, level off (~0.1 M) are expected to have no significant effect on the rate of C-Cl bond cleavage.



Figure 3: Reduction potentials (blue) and rate constants (orange) of SmI_2 for benzyl chloride as function of EG concentration.

The two types of behavior exhibited by anthracene and benzyl chloride suggest that plots similar to those presented in Figures 2 and 3 may serve as a reliable diagnostic tool to identify the ratedetermining step in the reactions of SmI_2 .

In order to further support the validity of the concept, it is worthwhile to consider the kinetics of a general substrate for which protonation is rate determining (Eq. 2). Assuming a steady state concentration of radical anion, the kinetics of the reaction is described by Equation 3.

Substrate + Sml₂
$$\xrightarrow{k_{et}}$$
 Substrate \cdot Sml₂ $\xrightarrow{k_p}$ Substrate H (2)

$$k_{obs} = \frac{k_{et} \cdot k_p}{k_{-et} + k_p} \tag{3}$$

If k_p is increased so that $k_p \gg k_{-et}$, k_{obs} becomes equal to k_{et} , which is expected to respond to changes in the concentration of EG similarly to the reduction potential, as observed for benzyl chloride (Fig. 3). Such a change from anthracene to benzyl chloride behavior is expected to occur gradually,

along with an increase in the protonation rate. However, since we cannot enhance the protonation rate on anthracene, another substrate, cyclohexanone, was employed, which undergoes protonation on the oxygen, a process known to be much faster than protonation on carbon.¹³ For comparison, we use normalized plots (where the maximum value is set to be 1) as shown in Figure 4, which demonstrates that the curve for cyclohexanone has indeed moved in the expected direction relative to anthracene.



Figure 4: Normalized graphs of SmI_2 reduction potentials (blue), rate constants with anthracene (orange), and rate constants with cyclohexanone (red) as function of EG concentration.

Figure 5 shows the same type of graph for the ligand NMEA, which increases the reduction potential of SmI₂ much more than EG (Table S1),^{6a} reacting with anthracene and 3-methyl-2-butanone. The figure clearly shows that the gap observed for anthracene shrinks significantly with 3-methyl-2-butanone as a substrate, in line with our suggestion. Needless to say, the rate constants for benzyl chloride match very well with the reduction potentials (Figure S5). It is concluded from Figures 4 and 5 that the faster the protonation, the smaller the gap between the two curves.



Figure 5: Normalized graphs (maximum value taken as 1) of reduction potential (blue), rate constants with anthracene (orange), and rate constants with 3-methyl-2-butanone (red) as function of NMEA concentration.

Finally, at the suggestion of a referee to examine the effect of the anions associated with Sm^{2+} which is often over looked, we have studied the effect of EG on the $\text{Sm}(\text{OTf})_2^{14}$ reactions with benzyl chloride and anthracene. First, we have compare the rate of reduction of these two presentative substrates by SmI_2 and $\text{Sm}(\text{OTf})_2$ in the presence of EG as additive. As evident clearly from Figure S8 and S9 (numerical values of rate constants are given in Table S4), that effect of EG on the reaction of $\text{Sm}(\text{OTf})_2$ is very similar to SmI_2 . In addition, rates of benzyl chloride reduction by SmI_2 and $\text{Sm}(\text{OTf})_2$ in the absence of EG are also very close, which suggests that reduction potential of these two Sm(II) salts are comparable.

With this mechanistic understanding at hand, we have applied above discussed diagnostic tool in $Sm(OTf)_2$ mediated reactions (Figure 6). To construct these plots, we have used reduction potential values of SmI_2 . Overall, these results show that the same behavior is obtained regardless of whether the counter ion is iodide or triflate suggesting that, at least in this case, the anions associated with the samarium cation are either bystander spectators or that the role they play in the reaction is not much dependent on their identity. It could be of interest to broaden the scope of this paper to other solvents such as DME. However, in doing so one must not transfer the data from THF to the other

solvent since the solvent coordination free energy to the SmI_2 and Sm^{3+} will change and therefore, will affect all the related parameters including the reduction potential.



Figure 6: Reduction potentials (blue) and rate constants (orange) of $Sm(OTf)_2$ for benzyl chloride as function of EG concentration. Insert shows similar plot using anthracene as substrate.

Conclusions.

In conclusion, we have shown that different levels of ligand coordination to SmI_2 are needed for the fulfillment of different tasks. Partial coordination is sufficient for reaching the maximal reduction potential of SmI_2 , concomitantly attaining the maximal rate of electron transfer. On the other hand, when the coordinated ligands play a role in the rate determining step of the reaction, for example when they protonate the radical anion, protonation is facilitated by completion of the coordination sphere at significantly higher ligand concentrations. Plots such as those shown in Figures 2 and 3 may serve as a very good diagnostic tool for assessing the role played by the ligands in the reaction.

A few words of caution: in the case of benzyl chloride, the rate determining step is the electron transfer, whereas in the reduction of anthracene, the electron transfer is a pre-equilibrium step, which is followed by a rate determining proton transfer. It should be emphasized that it is possible that a reaction may exhibit a benzyl chloride-like behavior, and yet the electron transfer can still be reversible. This case will be encountered if the rate determining step is independent of the

ligands surrounding the SmI₂, for example if the rate determining step is cyclization. The kinetic equation then becomes similar to Eq. 2, with k_{cvc} replacing k_p (Eq. 4):

$$k_{obs} = \frac{k_{et} \cdot k_{cyc}}{k_{-et} + k_{cyc}} \tag{4}$$

When $k_{cvc} \ll k_{-et}$, it will be reduced to Equation 5:

$$k_{obs} = \frac{k_{et}}{k_{-et}} k_{cyc} = K_{et} \cdot k_{cyc}$$
(5)

Since k_{cyc} is independent of the abundance of ligands around the Sm³⁺, and as K_{et} is related to the reduction potential in a similar manner as k_{et} , this case will also exhibit a benzyl chloride-like behavior, although electron transfer is not rate determining.

The second point to be considered is the recent suggestion that SmI_2 reacts with anthracene in the presence of water by a hydrogen atom transfer (HAT) mechanism (Eq. 6)^{2i,15} which is sometimes referred to as proton-coupled electron transfer (PCET).

$$\underbrace{\operatorname{Sml}_{2} \bullet \operatorname{H}_{2} O}_{\cdot} \underbrace{\operatorname{H}_{+} \operatorname{H}}_{\cdot} (6)$$

In this case, the rate determining step is also the first step, as the electron and proton transfer steps are coupled into a single step. The behavior may be similar to that observed for anthracene, rather than for benzyl chloride, as the HAT depends also on the availability of protons around the SmI_2 , which in turn correlates with the number of ligand molecules that are attached to SmI_2 .

Experimental Section

General: All the reagents were purified prior to use by following standard procedures.¹⁶ Liquid reagents such as substrates and additives were degassed with argon prior to use. THF was dried and freshly distilled off sodium/benzophenone under argon atmosphere. SmI₂ was freshly prepared prior to use by stirring of samarium metal and 1,2-diiodoethane at room temperature.^{4d} The concentration of SmI₂ was determined by UV-visible spectroscopic measurements (λ 619 nm; ε = 635).^{6a} Kinetic reactions were carried out in clean and dry glassware under nitrogen atmosphere.

Kinetics and UV-VIS measurements: Stopped flow kinetic and UV-visible spectral measurements were carried out in a Hi-Tech Stopped Flow Spectrometer. In kinetic measurements, all the reactions were performed under pseudo first order conditions (SmI₂: 2 mM and Subs: 10 mM). Rate of reactions were monitored by following the disappearance of the SmI₂-additive complex absorbance. Reduction of anthracene, 3-methyl-2-butanone and cyclohexanone resulted 9,10-dihydroanthracene¹⁷, 3-methyl-2-butanol¹⁷ and cyclohexanol^{2h} respectively. Reduction of benzyl chloride provided mixture of toluene and 1,2-diphenylethane.¹⁷

Spectral measurements were performed with a Stopped Flow Spectrometer. To record the spectrum of SmI_2 in the presence of additives, SmI_2 and the corresponding additive were taken in two different syringes and mixed within the stopped flow machine. The wavelength was scanned over a range to obtain the spectrum. The concentration of SmI_2 in all the experiments was 2 mM.

Cyclic Voltammetry: Cyclic voltammetry was performed in a single potentiostat from Bio Logic Scientific Instruments. Glassy carbon, Ag/AgNO₃ in acetonitrile and Pt wire were used as working, reference and counter electrode, respectively. The glassy carbon electrode was polished with polishing alumina and then washed thoroughly before each set of measurements. The reference electrode had a potential of 0.542V with respect to SHE. Tetrabutylammonium hexafluorophosphate (0.1 M) was used as a supporting electrolyte. The SmI₂ concentration was 2 mM for all sets of experiments.

Supporting Information

Cyclic voltammetry data, rate constants of reductions, UV-vis spectra, additional CV vs kinetics plots and kinetic traces used to determine rate constants are provided in Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

Corresponding Author

*E-mail: shoz@biu.ac.il

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TOC graphics

