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Experimental and Theoretical Studies on Methanol Solvation  
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## ARTICLE

## Proton donor effects on the reactivity of $\text{SmI}_2$ . Experimental and Theoretical Studies on Methanol Solvation vs. Aqueous Solvation

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Proton donors are important components of many reactions mediated by samarium diiodide ( $\text{SmI}_2$ ). The addition of water to  $\text{SmI}_2$  creates a reagent system that enables the reduction of challenging substrates through proton-coupled, electron-transfer (PCET). Simple alcohols such as methanol are often used successfully in reduction of  $\text{SmI}_2$  but often have reduced reactivity. The basis for the change in reactivity of  $\text{SmI}_2\text{-H}_2\text{O}$  and  $\text{SmI}_2\text{-MeOH}$  is not apparent given the modest differences between water and methanol. A combination of Born-Oppenheimer molecular dynamics simulations and mechanistic experiments were performed to examine the differences between the reductants formed *in situ* for the  $\text{SmI}_2\text{-H}_2\text{O}$  and  $\text{SmI}_2\text{-MeOH}$  systems. This work demonstrates that reduced coordination of MeOH to Sm(II) results in a complex that reduces arenes through a sequential electron proton transfer at low concentrations and that this process is significantly slower than reduction by  $\text{SmI}_2\text{-H}_2\text{O}$ .

### Introduction

Proton donors are an important component of reactions that employ samarium (II) diiodide ( $\text{SmI}_2$ ).<sup>1–5</sup> Examples of proton donors used in reactions of  $\text{SmI}_2$  and Sm(II)-based reagents include water, glycols, and alcohols. Although water has proven to be a unique proton donor in reactions of Sm(II), other proton donors have attractive aspects.<sup>6–9</sup> The addition of alcohols to reactions of  $\text{SmI}_2$  were first reported by Kagan and their presence was found to increase the rate and yield of substrate conversion.<sup>10</sup> In reactions that use proton donors other than water there are two types of alcohols used: coordinating and non-coordinating alcohols. Coordinating alcohols include methanol (MeOH) and ethanol (EtOH).<sup>1,4,11–14</sup> Alcohols containing larger or branched alkyl chains are not able to coordinate to Sm(II) due to steric hindrance. Examples of non-coordinating

alcohols include *n*-butanol (*n*-BuOH) and *tert*-butanol (*t*-BuOH). One attractive aspect of the use of alcohols is that in some cases, they can be utilized as an acceptable alternative to water. Although the large increase in reactivity that is observed with the addition of water to Sm(II) is not usually observed upon addition of alcohols, their presence is particularly useful when working under anhydrous conditions or with water-sensitive substrates.

A great deal of work has been performed to examine Sm(II)-alcohol systems, specifically by Hoz and coworkers. Studies by Hoz showed that the addition of methanol (MeOH) or *tert*-butanol (*t*-BuOH) led to both lower reactions times and higher yields in the reduction of a series of olefin-containing substrates. These systems were later studied more extensively including UV-vis experiments to probe alcohol coordination to  $\text{SmI}_2$ , product distribution, and isotopic labelling experiments. In these studies, it was observed that the effect of different alcohols on reactions of  $\text{SmI}_2$  was not the same.<sup>1,11,12</sup> Subsequent work by Flowers and coworkers provided the first rationalization for the variations among alcohol additives. In these studies, the reduction of acetophenone was explored using a series of alcohols and it was found that the  $\text{pK}_a$  of the alcohol additive directly correlated to the rate of reduction of acetophenone. This observation, along with steric effects to coordination provided a reasonable rationalization for the observed differences in alcohol additives.<sup>15</sup> Despite this previous work exploring the effects of different alcohols additives and the reasons for their observed differences in reactivity, one question that has not been adequately addressed is the large difference in reactivity

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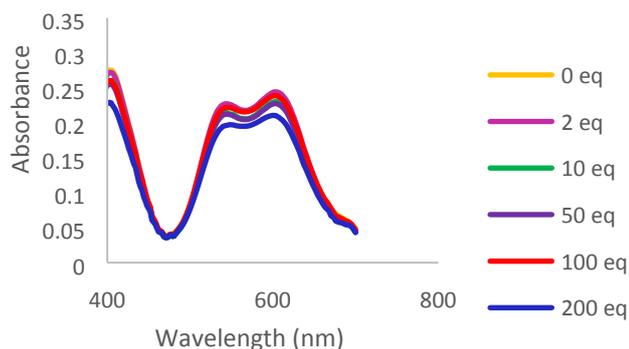
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between Sm(II)-water and Sm(II)-MeOH. In the former case, many reactions are significantly more efficient even though steric and  $pK_a$  differences are modest. Herein we examine the solvation environments of  $\text{SmI}_2$  in methanol vs. water through quantum chemical studies that provide accurate molecular pictures of these systems at room temperature. Additionally, rate studies are used to compare the reactivity of Sm(II)-water and Sm(II)-MeOH in the reduction of acenaphthene. These results reveal the importance of solvation and proton donor coordination to Sm(II) responsible for the mechanism of substrate reduction by the reagent systems.

## Results and Discussion

### A. Characterization of the $\text{SmI}_2$ -MeOH System

Various proton donors have been shown to have an affinity for Sm(II). Coordination to the Sm metal center can be probed using UV-vis spectrometry. To study the impact of the addition of MeOH to  $\text{SmI}_2$ , a series of UV-vis experiments were performed with increasing concentrations of MeOH versus a 2.5 mM solution of  $\text{SmI}_2$ . This is shown in Figure 1. A significant change is not observed in the spectrum until a large concentration of MeOH is achieved, well beyond those used under synthetically relevant conditions. This suggests that there is no significant coordination between MeOH and Sm(II) under conditions typically used in synthesis.<sup>11</sup>



**Figure 1.** UV-vis spectra of 2.5 mM  $\text{SmI}_2$  in THF containing 0, 2, 10, 50, 100, and 200 equiv of MeOH vs  $[\text{SmI}_2]$ .

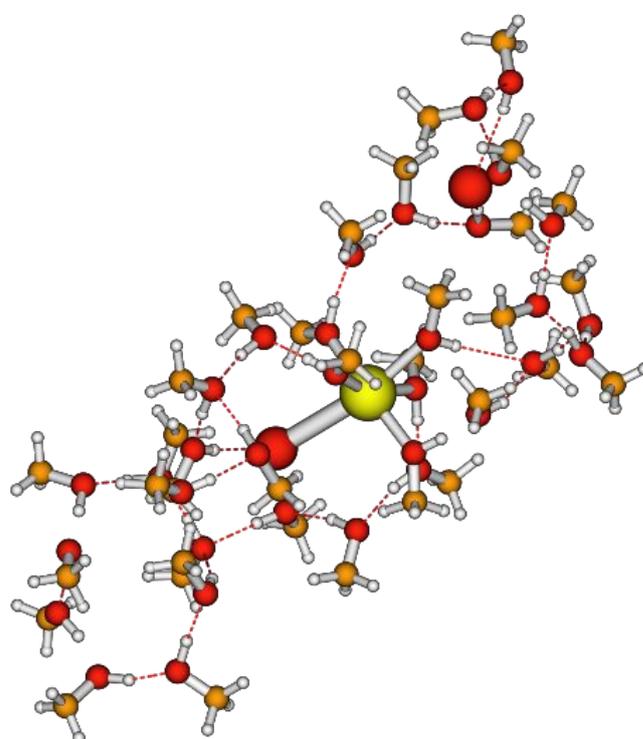
### B. Quantum chemical studies

Computational studies were performed on the  $\text{SmI}_2$ -MeOH system using Born-Oppenheimer molecular dynamics (BOMD) based on hybrid (M062X) Density Functional Theory (DFT) calculations. These calculations were performed using a  $\text{SmI}_2(\text{MeOH})_{32}$  microsolvation model. The BOMD simulations were carried out with Geraldyn-2.1<sup>16</sup> coupled to GAUSSIAN-09<sup>17</sup> at 300K. The NVT scheme used was identical to the one applied for other Sm(II) systems such as  $\text{SmI}_2(\text{H}_2\text{O})_{32}$ <sup>18</sup>,  $\text{SmBr}_2(\text{H}_2\text{O})_{32}$ <sup>19</sup>, and  $\text{SmCl}_2(\text{H}_2\text{O})_{32}$ <sup>20</sup>. The statistical results were then compared to those of the previously studied  $\text{SmI}_2(\text{H}_2\text{O})_{32}$  system. Specific details on the timestep, (C,O,H) atomic basis sets, the hybrid density functional, and the electronic structure and energy gradient calculations can be found in refs 12-14. The iodide and samarium atoms were treated with the 7 and 12 active valence

electrons Stuttgart-Köln relativistic effective core potentials in combination with their adapted valence basis sets, respectively.<sup>21,22</sup> An optimized structure of a  $\text{SmI}_2(\text{MeOH})_{25}$  seed was used as a starting point and this model was then surrounded by seven randomly located methanol molecules to start the simulation for the  $\text{SmI}_2(\text{MeOH})_{32}$  microsolvated model. The thermal energy using a Boltzmann distribution at 300 K was used to determine initial velocity vectors. The 25 ps (50000 system configurations) BOMD simulation on the lowest singlet potential surface took 12170 CPU days. A thermalization of 10 ps was used for these calculations. The last 15 ps of the trajectory was used to perform statistical analysis; structural, dynamic, and energetic data were extracted. The Sm-O, Sm-C, Sm-I radial distribution functions and coordination numbers (CN) were determined using the last 12 ps of the BOMD trajectory.

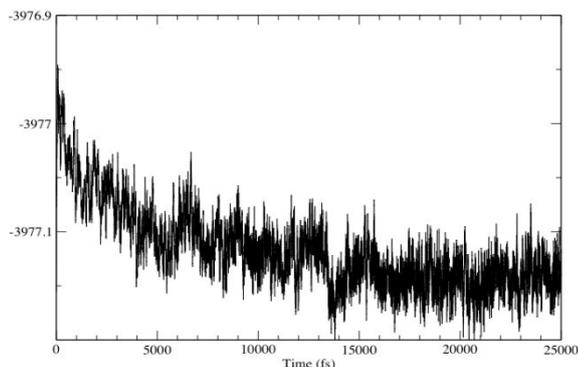
The EXAFS spectrum was obtained from the molecular dynamics trajectory using the same procedure that was used for the aqueous solvation of other Sm(II) systems such as  $\text{SmBr}_2$ <sup>19</sup>, and  $\text{SmI}_3$ <sup>23</sup>. Upon thermalization, the theoretical EXAFS spectrum was obtained using 500 decorrelated snapshots. In order to include methanol molecules whose oxygen atoms lie at a distance up to 5.5 Å, a cutoff center around the Sm atom was applied to each structure. Paths with lengths up to this value were included considering multiple scattering. The EXAFS calculations were performed using the FEFF program<sup>24</sup> (version FEFF85L) with an amplitude reduction factor  $S_0^2 = 1$ .

### C. Analysis of the BOMD Simulation



**Figure 2.** Typical microsolvation pattern for the  $\text{SmI}_2$ -(MeOH)<sub>32</sub> system at 300 K. Sm (yellow), oxygen (small red), carbon (orange) and iodides (large red).

A typical microsolvation pattern, after thermalization was achieved, for  $\text{SmI}_2$  in methanol can be seen in Figure 2. The evolution of the total potential energy during the entire simulation can be seen in Figure 3. Thermalization was attained in 26000 steps because the slope of the linear fit of the water binding energy for the last 12 ps is  $-1.2 \times 10^{-4}$  a.u./ps.

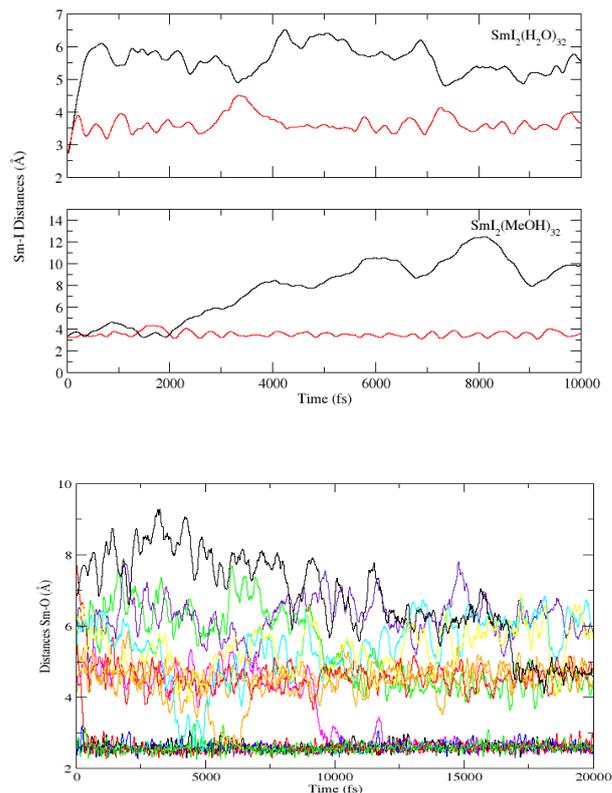


**Figure 3.** Evolution of the total potential energy (a.u.) for the  $\text{SmCl}_2\text{-(MeOH)}_{32}$  system at 300 K.

The evolution of the Sm-I and Sm-O distances of the  $\text{SmI}_2(\text{H}_2\text{O})_{32}$  and  $\text{SmI}_2(\text{MeOH})_{32}$  systems can be directly compared (Figure 4) because the BOMD simulations were performed using the same conditions<sup>12</sup>. A comparison of these plots shows that there is a significant difference in the behavior of the halogens with respect to the Sm(II) metal center under the same microsolvation conditions. In the  $\text{SmI}_2$ -water system a rapid dissociation of both Sm-I bonds is observed. In this system, one of the iodide ions oscillates between the first and second water solvation shells. (ca. 3.6 Å) and the other is ejected past the second solvation shell and remains at an average distance of 5.5 Å. The free space left leads to a large coordination number for water, CN= 8.5 around Sm(II).

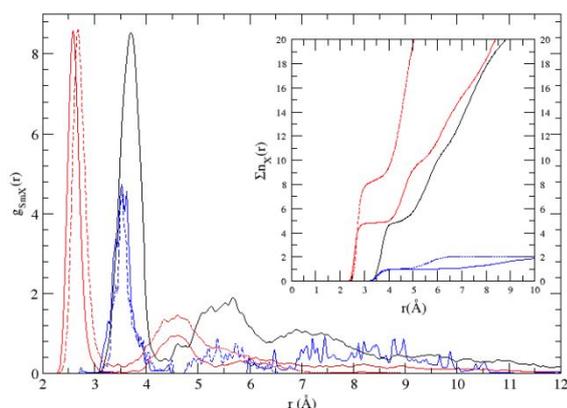
Upon the addition of methanol to  $\text{SmI}_2$ , one of the iodide ions is ejected from the Sm(II) coordination sphere and becomes solvated by methanol. However, the other iodide remains tightly bonded to Sm and both anions are solvated by H(O). The lone pairs on the oxygen in the methanol molecules allow them to interact with Sm(II) in the first coordination shell.

Radial distribution functions can be seen in Figure 5. The Sm-O, Sm-I RDFs are compared with those obtained in water. In the  $\text{SmI}_2$ -MeOH system the first solvation shell extends from 3 to 4.2 Å and its integration leads to a small coordination number for methanol of five (CN=5) molecules around the Sm(II) cation. This is a significant decrease from the  $\text{SmI}_2$ -water CN=8.5.



**Figure 4 .** Evolution of the Sm-O (above) and Sm-I (below) distances for the  $\text{SmI}_2\text{-(MeOH)}_{32}$  system at 300K. The two Sm-I distances are shown (red/ black) and note the different scales. Only five methanol molecules define the first solvation shell. Only the 12 smaller Sm-O distances are shown for clarity.

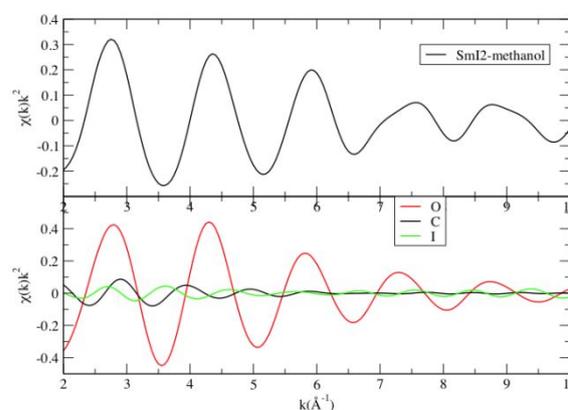
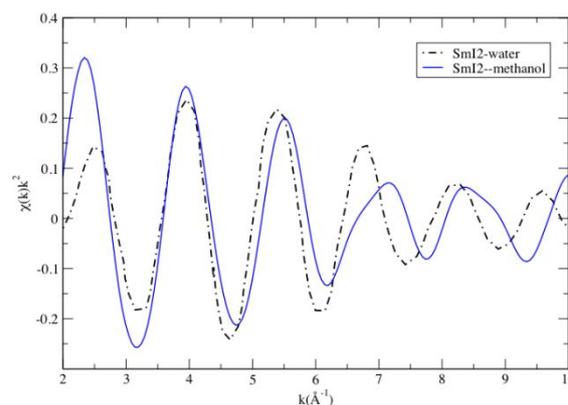
This smaller number of molecules in the first Sm(II)-solvation shell arises due to steric effects introduced by the bulkier methanol molecules. The second solvation sphere extends from 4 to ca 6.3 Å, with a slight shoulder found at 6.0 Å that is indicative of the superposition of the second and third solvation shells. For the  $\text{SmI}_2$ -MeOH system, it is clear that there is a much less well defined solvation structure around the Sm(II) than what is found with water.



**Figure 5.** Sm-X radial distribution functions with X=O (red), C (black) and I (blue). Solid lines are used for  $\text{SmI}_2\text{-(MeOH)}_{32}$  system while dashed lines are used for  $\text{SmI}_2\text{-(H}_2\text{O)}_{32}$ . In the inset the corresponding coordination numbers are shown.

The theoretical EXAFS spectrum is shown in Figure 6. To the best of our knowledge there is no experimental EXAFS spectrum reported for  $\text{SmI}_2$  in methanol. Therefore, only a qualitative comparison can be made to our theoretical prediction that was obtained for the  $\text{SmI}_2\text{-water}$  system.

The significant role that the methyl groups play in the overall EXAFS spectrum of  $\text{SmI}_2(\text{MeOH})_{32}$  can be seen in Figure 6. The presence of the methyl groups leads to large differences between the EXAFS spectrum of  $\text{SmI}_2(\text{MeOH})_{32}$  and  $\text{SmI}_2(\text{H}_2\text{O})_{32}$  resulting in an amplitude for the  $\text{SmI}_2(\text{MeOH})_{32}$  system that is much larger in the small wavenumber region. In the large  $k$  domain, an odd decay shape can be seen between  $6\text{-}9 \text{ \AA}^{-1}$ , which is perhaps mainly due to the interference of oxygen and carbon scattering signals in the first solvation shell (see the maxima in the Sm-O and Sm-C RDF between 3 and  $4.5 \text{ \AA}$  in figure 5). These data show key differences between the  $\text{SmI}_2\text{-methanol}$  system and the  $\text{SmI}_2\text{-water}$  systems. These differences are explained in terms of the different local dynamic solvation patterns for  $\text{SmI}_2\text{-methanol}$  vs.  $\text{SmI}_2\text{-water}$ . These different local solvation environments can be explained by the much larger steric effect between neighboring methanol molecules close to the metal center, which leads to a much lower coordination number (CN=5) for the  $\text{SmI}_2\text{-MeOH}$  in comparison to the  $\text{SmI}_2\text{-water}$  system (CN=8.5). These values can be seen in Table 1. The impact on the reactivity of  $\text{SmI}_2\text{-methanol}$  in comparison to  $\text{SmI}_2\text{-water}$  given the differences in solvation and speciation are discussed in the following section.



**Figure 6.** a) EXAFS spectra for the microsolvated  $\text{SmI}_2\text{-(MeOH)}_{32}$  and  $\text{SmI}_2\text{-(H}_2\text{O)}_{32}$  systems at 300 K. b) Lower panel shows the contribution of each type of atom to the total  $\text{SmI}_2\text{-(MeOH)}_{32}$  EXAFS signal.

**Table 1.** Average Sm-I distances and water/methanol coordination numbers (CN) for the  $\text{SmI}_2\text{-(solvent)}_{32}$  systems.

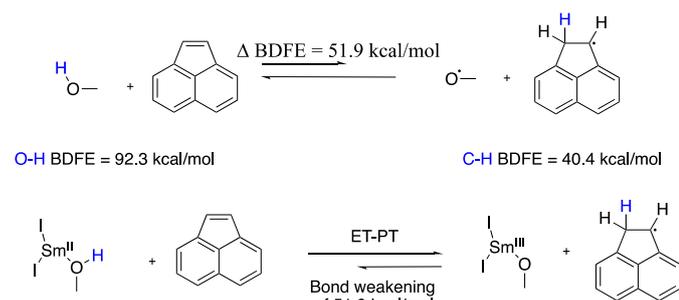
$\text{SmI}_2\text{-solvent}$ system	Average Sm-I ( $\text{\AA}$ )	CN
$\text{SmI}_2\text{-(MeOH)}_{32}$	5.72	5.0
$\text{SmI}_2\text{-(H}_2\text{O)}_{32}$	4.67	8.5

#### D. $\text{SmI}_2\text{-methanol}$ reagent studies

Given the differences in solvation of  $\text{SmI}_2$  in water and MeOH we explored the reducing capabilities of each reagent system. Previous work in our group has shown that kinetic studies along with synthetic studies of a series of arene reductions can be used to estimate the limits of bond weakening for Sm(II)-proton donor complexes and establish the probable mechanism of reduction.<sup>9</sup> After examining the reduction of several arenes, we established that the limit of reduction for  $\text{SmI}_2\text{-MeOH}$  in THF was acenaphthylene. Density functional theory (DFT) calculations were performed as described in previous works to determine bond dissociation free energies (BDFEs) of the intermediate

radicals that would be formed upon a hydrogen atom transfer (HAT) to acenaphthylene in THF.<sup>25,26</sup> The minimum degree of bond weakening for this radical intermediate to be formed can therefore be determined by subtracting the O–H BDFE from the C–H BDFE of the radical formed upon hydrogen atom transfer to acenaphthylene. If weakening of the O–H bond of methanol occurs upon coordination to  $\text{SmI}_2$ , this experiment demonstrates a reduction of the bond strength of 51.9 kcal/mol (Scheme 1). This bond weakening is significantly smaller than the amount previously reported for water bound to  $\text{SmI}_2$  of 72.7 kcal/mol.<sup>8</sup>

**Scheme 1.** Approximation of the Minimum Degree of O–H bond weakening upon coordination of methanol to  $\text{SmI}_2$  in THF



The thermodynamic analysis shown in Scheme 1 demonstrates the limit of bond-weakening for  $\text{SmI}_2$ -MeOH, but not the mechanism. Previous work has demonstrated that the addition of alcohols to  $\text{Sm(II)}$  lead to reduction through a sequential mechanism where proton transfer occurs after a rate-limiting ET.<sup>18</sup> To further investigate the mechanism of reduction for the  $\text{SmI}_2$ -MeOH system, kinetic studies were performed, and rate orders were determined for each of the components. Rate studies were performed under initial rates conditions with acenaphthylene,  $\text{SmI}_2$  and MeOH under synthetically relevant conditions. Reaction kinetics were monitored using stopped-flow spectrophotometry to observe the decrease of absorbance of  $\text{SmI}_2$  at 560 nm. Methanol concentrations were varied over a range from 0.06 M to 0.18 M and 1 M, with constant concentrations of  $\text{SmI}_2$  and substrate. Each measurement was repeated thrice with freshly prepared samples. Rate orders for  $\text{SmI}_2$ , substrate, and MeOH can be found in Table 2. The rate order of  $\text{SmI}_2$  is near unity. The rate order of substrate is positive, but less than unity and likely a consequence of aggregation. Overall the rate order of MeOH is approximately 0 showing negligible variation at low concentrations within the natural decay of  $\text{SmI}_2$  in the absence of substrate. This is indicative of methanol not being involved in the rate-determining step of the reaction at low concentration. This supposition is further supported by previous work by Procter which demonstrated a 53% reduction of acenaphthylene by  $\text{SmI}_2$  in the absence of a proton donor.<sup>27</sup> Since the reduction of substrate occurs very slowly, these results are consistent with an initial ET being rate limiting. However, it is possible that at high concentrations of MeOH, a rate limiting PT or PCET may be possible due to coordination between Sm and MeOH that changes the mechanism of the reaction. This supposition is supported by the classic work of Cuerva and

coworkers who demonstrated that the reduced affinity of MeOH (compared to water) for low-valent titanocene, is responsible for titanocene-water being a better formal hydrogen atom donor than titanocene-MeOH.<sup>28</sup>

**Table 2:** Rate Orders for the Reduction of Acenaphthylene by  $\text{SmI}_2$ -MeOH

Reaction Component	Rate Order
$\text{SmI}_2$	$0.8 \pm 0.1^a$
MeOH	0 <sup>b</sup>
Acenaphthylene	$0.6 \pm 0.05^c$

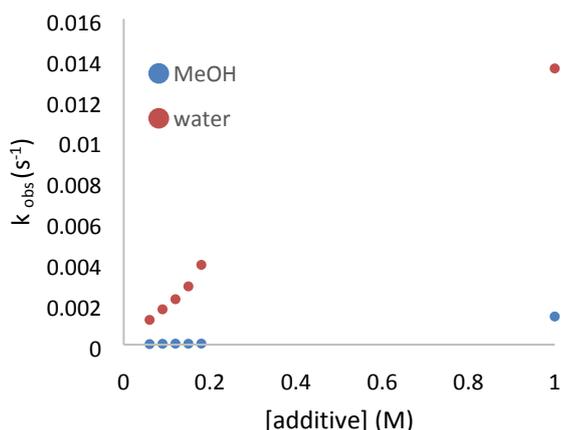
Conditions: <sup>a</sup>Initial rates method. 60 mM MeOH, 2 mM acenaphthylene, 0.004–0.012 M  $\text{SmI}_2$ . <sup>b</sup>order of methanol showed negligible variation over the concentration range studied until reaching a concentration of 1M where MeOH began to impact the rate. <sup>c</sup>6 mM  $\text{SmI}_2$ , 60 mM MeOH, 2–10 mM acenaphthylene. The rate orders are the average of three independent experiments.

**Table 3:** Rate Orders for the Reduction of Acenaphthylene by  $\text{SmI}_2$ -water.

Reaction Component	Rate Order
$\text{SmI}_2$	$0.9 \pm 0.07^a$
Water	$2.0 \pm 0.1^b$
Acenaphthylene	$0.5 \pm 0.02^c$

Conditions: <sup>a</sup>Initial rates method. 60 mM  $\text{H}_2\text{O}$ , 2 mM acenaphthylene, 0.004–0.012 M  $\text{SmI}_2$ . <sup>b</sup>6 mM  $\text{SmI}_2$ , 60–180 mM  $\text{H}_2\text{O}$ , 2 mM acenaphthylene. <sup>c</sup>6 mM  $\text{SmI}_2$ , 60 mM  $\text{H}_2\text{O}$ , 2–10 mM acenaphthylene. The rate orders are the average of three independent experiments.

Kinetic experiments were performed on the reduction of acenaphthylene using the  $\text{SmI}_2$ -water system to compare with the  $\text{SmI}_2$ -MeOH reagent system. When rates of the two reagent systems are compared, the reduction of acenaphthylene by  $\text{SmI}_2$ -water proceeds at a rate that is several orders of magnitude faster than the reduction mediated by  $\text{SmI}_2$ -MeOH (Table 3 and Figure 7). The dramatic difference in rates observed between a coordinating proton donor capable of facilitating a PCET mechanism, such as water, and a modestly coordinating proton donor such as methanol demonstrates that reduction of acenaphthylene by  $\text{SmI}_2$ -MeOH proceeds *via* a sequential mechanism where the rate is impacted very little by  $[\text{MeOH}]$ .<sup>18</sup> However, it is important to note that at high concentrations of MeOH where the rate begins to increase, a change in mechanism may occur where a rate limiting PT or PCET may be likely due to ligand coordination of MeOH to  $\text{Sm(II)}$ .



**Figure 7.** Rate comparison of the reduction of 2 mM acenaphthylene by 6 mM SmI<sub>2</sub> using MeOH and water as proton donors.

Although the SmI<sub>2</sub>-MeOH combination provides a useful reducing system, it is substantially less reactive compared to the SmI<sub>2</sub>-H<sub>2</sub>O reagent system.<sup>2,29,30</sup> This is likely a consequence of the decrease in coordination number, with CN=5 for MeOH vs. 8.5 for water (note also that methanol can only provide a single O-H proton while water has two). The decrease in coordination leads to a sequential mechanism rather than a PCET mechanism which the SmI<sub>2</sub>-H<sub>2</sub>O system has been shown to proceed through, resulting in a drastic decrease in reaction rate.

## Conclusions

Herein we examined the similarities and differences using methanol as a proton donor vs. water for SmI<sub>2</sub>. The steric interaction between methanol molecules in the first solvation shell lead to a much smaller Sm-coordination number of 5 as compared to 8.5 found when water is used as solvent. The present results demonstrate that the addition of methanol to SmI<sub>2</sub> results in a reagent system that reduces substrates through a sequential mechanism at low concentrations of the proton donor. Methanol does not coordinate as strongly to Sm(II) as water and as a consequence, weakening of the O-H bond of methanol bound to Sm(II) is diminished at low concentrations precluding reduction through PCET. The increase in the rate of substrate reduction at high concentrations of MeOH (1M) demonstrates that a change in mechanism occurs when coordination commences leading to a rate limiting PT or PCET. We are currently examining a range of proton donors to examine more fully the relationship between coordination to Sm(II) and the mechanism of substrate reduction.

## Conflicts of interest

There are no conflicts to declare.

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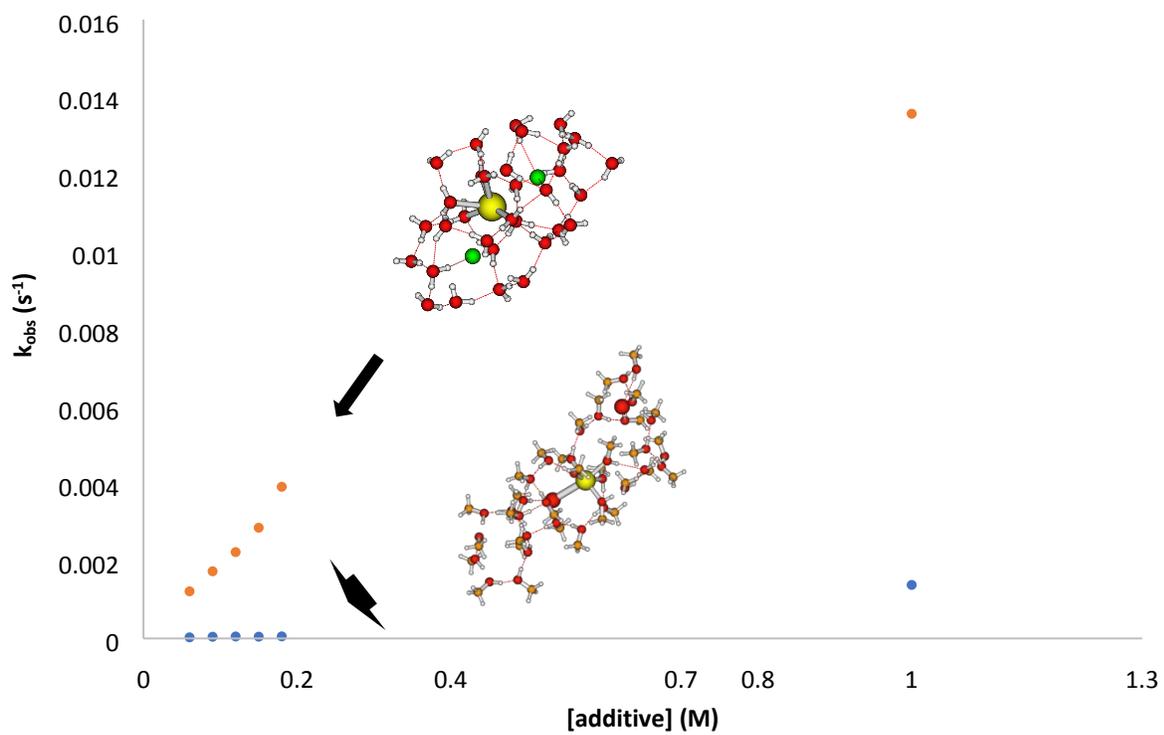
## References

- 1 M. Amiel-Levy and S. Hoz, *J. Am. Chem. Soc.*, 2009, **131**, 8280–8284.
- 2 S. S. Kolmar and J. M. Mayer, *J. Am. Chem. Soc.*, 2017, **139**, 10687–10692.
- 3 P. R. Chopade, E. Prasad and R. A. Flowers, *J. Am. Chem. Soc.*, 2007, **126**, 44–45.
- 4 J. A. Teprovich, M. N. Balili, T. Pintauer and R. A. Flowers, *Angew. Chemie - Int. Ed.*, 2007, **46**, 8160–8163.
- 5 T. V. Chciuk, W. R. Anderson and R. A. Flowers, *Angew. Chemie - Int. Ed.*, 2016, **55**, 6033–6036.
- 6 E. Prasad and R. A. Flowers, *J. Am. Chem. Soc.*, 2005, **127**, 18093–18099.
- 7 T. V. Chciuk, W. R. Anderson and R. A. Flowers, *J. Am. Chem. Soc.*, 2016, **138**, 8738–8741.
- 8 T. V. Chciuk and R. A. Flowers, *J. Am. Chem. Soc.*, 2015, **137**, 11526–11531.
- 9 C. O. Bartulovich and R. A. Flowers, *Dalt. Trans.*, 2019, **48**, 16142–16147.
- 10 P. Girard, J. L. Namy and B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693–2698.
- 11 A. Yacovan, S. Hoz and I. Bilkis, *J. Am. Chem. Soc.*, 1996, **118**, 261–262.
- 12 S. K. Upadhyay and S. Hoz, *J. Org. Chem.*, 2011, **76**, 1355–1360.
- 13 A. Tarnopolsky and S. Hoz, *Org. Biomol. Chem.*, 2007, **5**, 3801–3804.
- 14 A. Tarnopolsky and S. Hoz, *J. Am. Chem. Soc.*, 2007, **129**, 3402–3407.
- 15 P. R. Chopade, E. Prasad and R. A. Flowers, *J. Am. Chem. Soc.*, 2003, **126**, 44–45.
- 16 J.-P. D. and F. J. Christophe Raynaud, Laurent Maron, *Phys. Chem. Chem. Phys.*, 2004, 4226–4232.
- 17 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, .
- 18 A. Ramírez-Solís, C. O. Bartulovich, T. V Chciuk, J.

## Journal Name

## ARTICLE

- Hernández-Cobos, H. Saint-Martin, L. Maron, W. R. Anderson, A. M. Li and R. A. Flowers, *J. Am. Chem. Soc.*, 2018, **140**, 16731–16739.
- 19 A. Ramírez-Solís, J. I. Amaro-Estrada, J. Hernández-Cobos and L. Maron, *J. Phys. Chem. A*, 2017, **121**, 2293–2297.
- 20 A. Ramírez-Solís, C. O. Bartulovich, C. I. León-Pimentel, H. Saint-Martin, W. R. Anderson and R. A. Flowers, *Inorg. Chem.*, 2019, **58**, 13927–13932.
- 21 A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuß, *Mol. Phys.*, 1993, **80**, 1431–1441.
- 22 M. Dolg, H. Stoll, H. Preuss and R. M. Pitzer, *J. Phys. Chem.*, 1993, **97**, 5852–5859.
- 23 A. Ramirez-Solis, J. I. Amaro-Estrada, J. Hernández-Cobos and L. Maron, *Inorg. Chem.*, 2018, **57**, 2843–2850.
- 24 J. J. Rehr, J. J. Kas, F. D. Vila, M. P. Prange and K. Jorissen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5503–5513.
- 25 A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani and K. Throssell, *J. Chem. Theory Comput.*, 2012, **8**, 4989–5007.
- 26 R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, 1989.
- 27 M. Szostak, M. Spain and D. J. Procter, *J. Org. Chem.*, 2014, **79**, 2522–2537.
- 28 M. Paradas, A. G. Campaña, T. Jiménez, R. Robles, J. E. Oltra, E. Buñuel, J. Justicia, D. J. Cárdenas, and J. M. Cuerva, *J. Am. Chem. Soc.*, 2010, **132**, 12748–12756.
- 29 A. Dahlen and G. Hilmersson, *Eur. J. Inorg. Chem.*, 2004, 3393–3403.
- 30 X. Just-Baringo, C. Morrill and D. J. Procter, *Tetrahedron*, 2016, **72**, 7691–7698.



Using both computational and experimental data the SmI<sub>2</sub>-MeOH system is directly compared to the SmI<sub>2</sub>-H<sub>2</sub>O system to uncover the basis for their drastic differences in reactivity,