Proton-Coupled Electron Transfer in the Reduction of Carbonyls by Samarium Diiodide−Water Complexes

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⑤ *Supporting Information*

ABSTRACT: Reduction of carbonyls by SmI_2 is significantly impacted by the presence of water, but the fundamental step(s) of initial transfer of a formal hydrogen atom from the SmI_2−water reagent system to produce an intermediate radical is not fully understood. In this work, we provide evidence consistent with the reduction of carbonyls by SmI_2−water proceeding through proton-coupled electron transfer (PCET). Combined rate and computational studies show that a model aldehyde and ketone are likely reduced through an asynchronous PCET, whereas reduction of a representative lactone occurs through a concerted PCET. In the latter case, concerted PCET is likely a consequence of significantly endergonic initial electron transfer.

Reduction of a carbonyl by samarium diiodide (SmI_2) is the first step in a number of reductions and bond-forming reactions of synthetic importance.[1] Frequently reactions require use of additives to facilitate the initial reduction step.[2] Lewis bases such as HMPA and proton donors including alcohols and water are most often employed as additives to accelerate carbonyl reductions. Among these additives, water is unusual in that it enables the reduction of carbonyls that are recalcitrant to electron transfer (ET). Over the last several decades, a number of groups, most notably Procter, have shown that the SmI_2−water reagent system is capable of reducing lactones, Meldrum's acid derivatives, and related functional groups.[3] The key feature of these reactions is the reduction of substrates that have a significantly more negative reduction potential than SmI_2−water, making a process that proceeds through an initial ET significantly endergonic. Given the barrier to an initial ET, we questioned whether reductions by SmI_2−water occurred through an initial ET followed by a proton transfer (PT) or whether reduction occurred through a formal hydrogen atom transfer (HAT). To initially study this problem, we examined the reduction of anthracene by SmI_2−water. This substrate was chosen since it does not coordinate to SmI_2 enabling us to simplify the mechanistic analysis and focus on the interplay between the impact of water on the reducing power of the $Sm(II)$−water complex and the rate of reduction in the absence of substrate coordination.[4] This study showed that anthracene reduction occurred through an initial proton-coupled electron-transfer (PCET). The noteworthy aspect of the transformation was the significant weakening of the O−H bond of water upon coordination to $Sm(II)$. Follow-up studies utilizing other proton donors including ethylene glycol and diethylene glycol

demonstrated that strong chelation was critical for promoting reduction through PCET.[5]

In considering the reduction of a carbonyl, there are several other factors that can potentially influence the mechanism of reduction by SmI_2−water. First, since Sm is oxophilic, carbonyls have a high affinity for the metal, and this can likely impact the mechanism of reduction by SmI_2−water due to competitive coordination between substrate and proton donor. Second, although redox potentials of SmI_2 and ketones predict an endergonic ET, many aldehydes and ketones are reduced in the absence of additives. An elegant study by Farran and Hoz demonstrated that a significant portion of the driving force for electron transfer from $Sm(II)$ to activated ketones in the absence of a proton donor is a consequence of the strong Coulombic attraction between the ketyl and $Sm(III)$ providing a driving force of up to 25 kcal/mol.[6] These observations suggest that the mechanism of reduction of carbonyls is likely more complicated than the reduction of an arene by SmI_2−water.

To evaluate the mechanism of carbonyl reduction by SmI_2−water, we examined three substrates, heptaldehyde (**I**), cyclohexanone (**II**), and 5-decanolide (**III**). These substrates were chosen because they have carbonyls spanning a range of redox potentials that are known to be reduced by SmI_2−water. Rate studies on each substrate were carried out under pseudo-first-order conditions with substrate in at least a 10-fold excess to [SmI_2]. Water concentrations were examined over a range of 50 mM to 7 M. Each rate measurement was repeated a minimum of three times to examine reproducibility. A representative plot of k_{obs} vs [H_2O] for the reduction of **III** is shown in Figure 1.

Inspection of the data in Figure 1 shows that the rate of reduction increases until an apex at approximately 1.5 M water and the rate then decreases at higher concentrations of water. Additionally, the rate plot showed curvature consistent with a rate order of water greater than unity as demonstrated in previous studies on the reduction of anthracene (Supporting Information).[4,5] Similar behavior was observed for substrates **I** and **II** with the maximal rate of substrate reduction occurring at higher concentrations of water (See Supporting Information). To further examine the system, rate orders and constants were determined for each substrate. Studies were carried out up to 1 M water since this is the concentration range used in the majority of carbonyl reductions by SmI_2−water. The data are contained in Table 1.

For each substrate reduction examined, the rate order of SmI_2 and substrate were approximately one and water was second
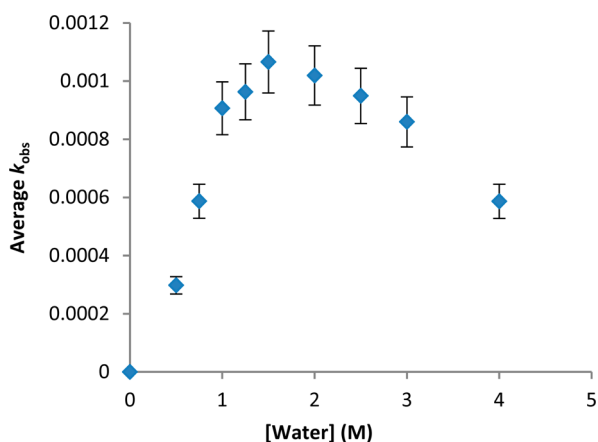
Figure 1. Plot of k_{obs} vs $[H_2O]$ for the reduction of **III** (500 mM) by SmI_2 (10 mM) at 25 °C.

Table 1. Rate Orders for Substrate Reduction by SmI_2−Water

substrate	rate constant (M^{-3} s^{-1})	rate orders		
		$H_2O^{a,d}$	substrate^b	$SmI_2{}^{c,d}$
I	$(4.2 \pm 0.3) \times 10^4$	2	1.0 ± 0.1	1
II	570 ± 70	2	1.1 ± 0.1	1
III	0.18 ± 0.01	2	0.9 ± 0.1	1

^{a}Conditions: pseudo-first order conditions with varying $[H_2O]$ (0−1 M) and constant $[SmI_2]$ (10 mM) and [substrate] (100 mM). ^{b}Conditions: pseudo-first order conditions with varying [substrate] (**I** = 100−160 mM, **II** = 100−500 mM, **III** = 400−800 mM) and constant $[SmI_2]$ (10 mM) and $[H_2O]$ (1 M). ^{c}Determined via fractional times method averaged over multiple trials. ^{d}[**III**] = 500 mM.

order. The fourth order rate constants spanned a range of 5 orders of magnitude with the rates of reduction **I** > **II** ≫ **III** correlating with substrate redox potential.[7] In the absence of water, **I** and **II** were reduced several orders of magnitude more slowly affording pinacols instead of reduced products; whereas **III** was not reduced, providing only recovered starting material.

To further examine the mechanistic impact of substrate reduction by water, a series of rate experiments were carried out employing D_2O in place of water. Rate measurements were obtained from the reduction of substrates using either water or D_2O at 1 M under pseudo-first order conditions with $[SmI_2]$ = 10 mM and substrate in a minimum 10-fold or greater excess. The k_H/k_D for substrates **I**, **II**, and **III** were determined to be 1.8 ± 0.1, 2.3 ± 0.1, and 1.7 ± 0.1, respectively. These values are somewhat different than those previously reported for similar reductions.[3c] In previous reported studies, KIEs were obtained from deuterium incorporation in products and attributed to a secondary isotope effect.[3c] Despite the fact that isotope effects were studied by different methods, the question is whether the k_H/k_D represents a primary or secondary effect. In reactions that involve PCET, isotope effects vary, and there are many examples where isotope effects are small.[8] In a classical ET−PT, a highly ordered early transition state would be expected to provide a low k_H/k_D since the zero point vibrational energy differences for D and H are small between the reactant and activated complex.[9] As a consequence, it is probable that the KIE obtained from independent rate experiments as described above are consistent with a primary isotope effect.

To acquire a more detailed understanding of the reduction of substrates **I**−**III** by SmI_2−water and further examine the basis for

deuterium isotope effects, rates of reduction were measured over a 30 K temperature range to obtain activation parameters for the reaction. For these experiments, water was maintained at 1 M (100 equiv) based on $[SmI_2]$ since this is the concentration where water exhibits a rate order of 2. During studies on the reduction of **I**, we were surprised to find that the rate of reduction slowed with increasing temperature. The Eyring plot for the reduction of **I** is displayed in Figure 2. The activation parameters
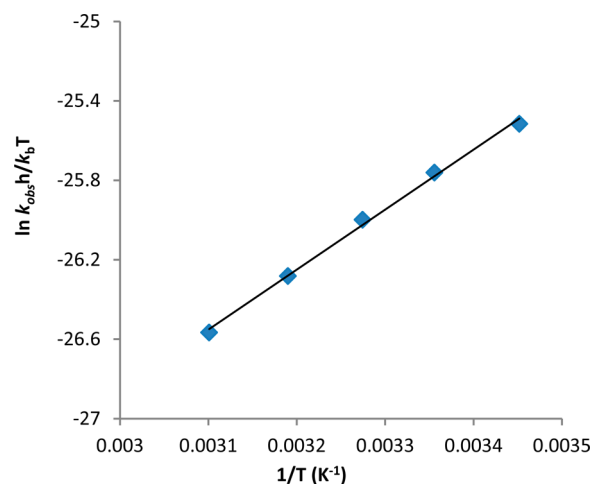

Figure 2. Eyring plot for the reduction of **I** (100 mM) by SmI_2 (10 mM) and water (1 M) over a range of 30 K.

Table 2. Activation Parameters for the Reduction of Substrates by SmI_2−Water^a

substrate	$\Delta H^{\ddagger b}$ (kcal mol^{-1})	$\Delta S^{\ddagger b}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger c}$ (kcal mol^{-1})
I	-6.1 ± 0.2	-72 ± 1	15.3 ± 0.1
II	-1.7 ± 0.3	-65 ± 1	17.8 ± 0.1
III	9.6 ± 0.1	-41 ± 1	21.7 ± 0.1

^{a}Conditions: 10 mM SmI_2, 1 M H_2O, and 100 mM **I** and **II** or 500 mM **III** in THF. The activation parameters are the average of three independent experiments from 293 to 323 K and are reported as $\pm\sigma$. ^{b}Obtained from $\ln(k_{obs}h/(k_bT)) - \Delta H^{\ddagger}/(RT) + \Delta S^{\ddagger}/R$. ^{c}Calculated from $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

for the reduction of **I**−**III** are contained in Table 2. We recognize that without a rigorous analysis, transition state parameters can be susceptible to systematic errors.[10] Nonetheless, comparison of the data provides important insight into the activation process for a series of related reactions. Evaluation of the $\Delta H^{\ddagger}$ for the reduction of substrates displays the trend **I** < **II** < **III** with **I** and **II** displaying negative enthalpies of activation and **III** providing a positive value for $\Delta H^{\ddagger}$. Negative enthalpies of activation are relatively rare, but several examples are known for systems involving PCET.[11] Negative values of $\Delta H^{\ddagger}$ are often ascribed to the presence of low concentrations of intermediates that are enthalpically favored.[11] All substrates display negative $\Delta S^{\ddagger}$ values with the trend being **I** < **II** < **III**. Overall, these data show that the low activation barrier for **I** and **II** is compensated by a substantial entropic cost in the activated complex. The consequences of this finding are discussed *vide infra*.

The data presented above show that the ease of substrate reduction (as measured by redox potential) correlates with the enthalpy of activation. This raises the interesting question, does

the formation of charge upon an initial ET from SmI$_2$−water stabilize the ketyl radical through the interaction between the ketyl oxygen and Sm(III) leading to a strong Coulombic attraction? If so, what are the differences among substrates I−III in the formal transfer of a hydrogen atom from SmI$_2$−water to each substrate? To further assess the relationship between substrate structure and charge on the neutral carbonyl and radical anion, calculations were performed on I−III and their associated radical anions using Gaussian09(1) programs employing the APF-D(2) hybrid DFT method and the 6-311+g(2d,p) basis set. Solvation values were calculated using the polarizable continuum model with integral equation formalism, IEFPCM, with tetrahydrofuran as the solvent. Charges were determined using natural population analysis (NPA).[12] Results for NPA are shown in Table 3.

Table 3. Natural Population Analysis for the Carbonyl Oxygens of Substrates I−III and Their Associated Radical Anions

substrate	NPA for carbonyl	NPA for radical anion	ΔNPA
I	−0.580	−0.895	−0.315
II	−0.610	−0.899	−0.289
III[a]	−0.642	−0.871	−0.229

[a]Calculations were performed on δ-valerolactone.

The charges on the carbonyl oxygen of I−III follow the expected trend with I having the least electron density on the carbonyl oxygen and III having the most. The distribution of the electron density on the radical anions of these compounds demonstrates that the greatest increase in charge occurs for I and the least occurs for III. It was our supposition that the change in electron density from the neutral compound upon reduction to the radical anion would correlate with the $\Delta H^{\ddagger}$ values if a Coulombic interaction between the carbonyl oxygen and Sm was important during the reduction. A plot of $\Delta H^{\ddagger}$ vs ΔNPA provides a correlation of 0.997 (see Supporting Information). While one should be cautious when evaluating a trend line based on three points, there is clearly a relationship between the change in charge on the carbonyl oxygen and the strength of the interaction between Sm and oxygen during the course of the reduction.

Overall, the studies presented above provide the following observations: (1) The rate of substrate reduction by SmI$_2$−water is I > II ≫ III. (2) In the absence of water, substrates I and II are reduced significantly more slowly by SmI$_2$ and III is not reduced even after extended periods of time. (3) All reductions are first-order in substrate and SmI$_2$ and second order in water (below 100 equiv). (4) All reductions proceed through highly ordered transition states. Additionally, I and II display negative $\Delta H^{\ddagger}$ values and exhibit the trend III > II > I. (5) The $\Delta H^{\ddagger}$ values correlate well with the change in charge on the carbonyl oxygen of each substrate as measured by NPA.

In addition to the current findings, it is useful to consider the results in the context of previous studies. It is well-established that water and carbonyls have a high affinity for Sm(II). Water coordinates strongly to Sm(II), and spectroscopic studies have shown evidence for coordination between the metal and low concentrations of the proton donor in bulk THF.[13] In addition, carbonyls are known to have a high affinity for Sm(II).[14] To further test this finding, we examined the UV−vis spectrum of a 2.5 mM solution of SmI$_2$ in THF containing increasing amounts of III (see Supporting Information). The spectra show evidence

of coordination with as little as 5 equiv of substrate providing additional support for carbonyl coordination to Sm(II). Overall, the collection of data demonstrates that it is probable that both water and carbonyl are coordinated to Sm during the course of the reduction. Previous studies have established that proton transfer from bulk water is unlikely,[4] so it is reasonable to assume that formal HAT occurs through a highly ordered activated complex with one or both waters bound to Sm(II) as shown in Scheme 1.

Scheme 1
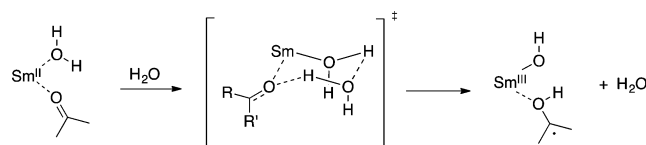
The question that remains is are these reactions a consequence of PCET? Reactions that proceed through PCET may be sequential or concerted.[15] In the former case, the transfer of an electron produces a stable intermediate that precedes proton transfer (or vice versa). In the latter instance, concerted PCET is favored when the stepwise pathways are significantly endergonic.[16] To further evaluate the process, it is instructive to consider the diagram displayed in Scheme 2. If a carbonyl is

Scheme 2
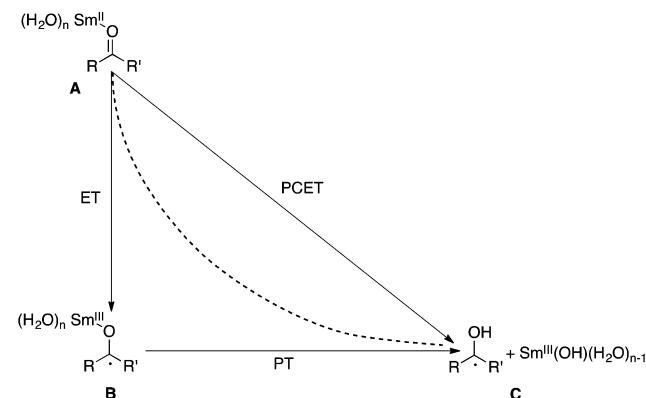
coordinated to the Sm(II)−water complex, **A**, a sequential process will produce intermediate **B**, followed by internal proton transfer to produce intermediate **C**. In a concerted process where the stepwise ET−PT is significantly endergonic, direct conversion from **A** to **C** occurs. It is reasonable to assume that a hybrid process is also possible (dotted line in Scheme 2). For instance, as reduction commences, increasing positive charge on Sm enhances the interaction between the emerging ketyl while simultaneously increasing the acidity of bound water promoting proton transfer.

In light of the data presented above and work described in previous studies, it is our supposition that in the case of substrates I and II, reduction occurs via asynchronous PCET that is driven by the stabilization of the developing charge through the Coulombically favored interaction of the carbonyl oxygen and Sm during the reduction. In the case of III, the activation barrier for reduction through an initial ET is highly endergonic. As a consequence, reduction of III proceeds through a concerted PCET from SmI$_2$−water.

Overall, the results and analysis contained herein provide evidence that formal hydrogen atom transfer from SmI_2–water to carbonyl occurs through PCET. The degree of stabilization achieved through a favorable Coulombic interaction between the carbonyl oxygen and Sm in the activated complex is a consequence of the degree of endergonicity of ET. While these studies clarify the mechanism of carbonyl reduction by SmI_2–water, the results may have implications for the activation and reduction or reductive coupling of other functional groups capable of coordinating to low valent metal–proton donor complexes.[17,18] We are currently examining a range of carbonyl functional groups and the impact of steric and electronic effects on reduction by SmI_2–water and other additives capable of promoting PCET from a complex with Sm(II). The results of these studies will be presented in due course.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05879.

General experimental methods and spectroscopic, rate, and computational data (PDF)

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Notes
The authors declare no competing financial interest.

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