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Broadening the Scope of Photostimulated SmI_2 Reductions

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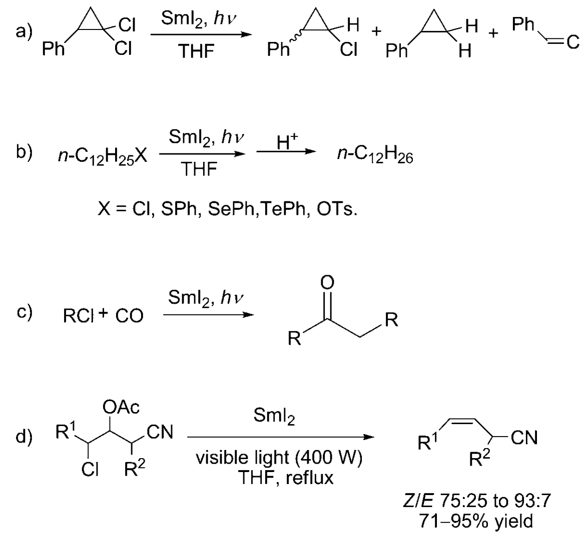
The electron-transfer process is the pivotal step in SmI_2 reductions.[1] In most cases, this step seems to be endothermic and slow. It could be enhanced by increasing the reduction potential of SmI_2, for example, by using additives such as hexamethylphosphoramide (HMPA).[2] Another way to increase the reduction potential of SmI_2 is by irradiation.[3] However, in contradistinction to the HMPA method, the range of applicability of this method is surprisingly limited. To the best of our knowledge, the reaction types shown in Scheme 1 are the only examples of the application of this method.[3]

Once the reason for the limited applicability of the photostimulation technique is understood, knowledge of the intimate mechanistic details of SmI_2 reactions may assist in the design of a strategy to broaden its scope.



Scheme 1. SmI_2 reduction under irradiation conditions. Ts = tosyl.

The common denominator for the photostimulated reactions shown in Scheme 1 is that there is no bimolecular rate-determining step following the electron transfer. These reactions involve either a dissociative electron attachment[4] process, such as in the mesolytic cleavage[5] of alkyl halides, or, as may be the case for C_6H_5X leaving groups, the radical anion may have a short lifetime before it either donates the electron back to the SmI_2 or undergoes cleavage. None of these reactions necessitate a bimolecular step, which should, for successful reaction, effectively compete with back electron transfer.

It should be noted that in the ground state there is no appreciable electron transfer from SmI_2 to the substrate in these cases. It is only after the SmI_2 is excited that the process becomes viable (excitation at around 600 nm is equivalent to approximately 2.2 eV, which is much more than the 0.72 V increase effected by HMPA (4 equiv).[6]) Yet, once electron transfer has taken place Sm^{3+} is no longer excited and, therefore, back electron transfer from the radical anion to the ground state of Sm^{3+} has a very high thermodynamic driving force. Hence, rapid back electron transfer prevents any bimolecular encounter, such as the protonation of the radical anion in the Birch-type reduction sequence[7] (electron–proton–electron–proton transfer).

The easiest way to overcome the deficiency of the extremely short lifetime of the radical anion caused by rapid back electron transfer is to convert the consequent bimolecular process, for example, protonation, into a unimolecular one. We have shown that the fact that MeOH complexes to SmI_2[8] enables protonation to occur from within the ion pair generated by electron transfer.[9] Protonation within the ion pair is a unimolecular process, which may therefore effectively trap the radical anion as it is formed and, therefore, the need for a bimolecular encounter between the short-lived radical anion and a proton donor from the bulk solution is rendered unnecessary. Herein, we show that exploiting this proximity effect[10] significantly broadens the scope of photostimulated SmI_2 reduction.

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In a preliminary test, we set up two UV cells containing naphthalene, SmI_2, and MeOH and exposed one to a simple UV lamp (UVSL-25; 254/366 nm) such as those used to locate spots on TLC plates, while the other was placed on the bench as a control under ordinary laboratory fluorescent lighting. In the event, the reaction in the cell under the UV lamp hardly progressed, whereas significant reaction took place in the cell on the bench. Moreover, significant reaction was observed when the same reaction was carried out with a mercury lamp and a filter that cuts off wavelengths below 600 nm. Since most of the synthetic SmI_2 reductions are carried out under laboratory lighting, chemists should be aware of the possibility that their reactions may, at least in part, be photostimulated.

We have employed two methods for the assessment of the photostimulated reactions. The first method was based on the fact that, in the diode array mode, the stopped flow spectrophotometer irradiates the sample continuously (in the single wavelength (SWL) mode, the cell is exposed to only a minute amount of irradiation).[11] Figure 1 shows the reactions of naphthalene with SmI_2 in the presence of MeOH or trifluoroethanol (TFE), an alcohol that does not complex to SmI_2.[9,12] In the presence of MeOH, a reaction time of 200 s corresponds to approximately two half-lives, whereas with TFE, following the disappearance of the SmI_2 after 800 s, revealed only natural decay.

The second method involves placing the UV cell with the reaction mixture (prepared in the glove box) 7.5 cm from the tip of a 450 W low-pressure mercury lamp for intervals of 20 s to 2 min (depending on the reaction rate) and measuring the absorption at the end of each interval.

Three substrates were studied: naphthalene, diphenylacetylene, and methylbenzoate. None of the three substrates reacted in the dark or in the light in the presence of TFE as the proton donor. With MeOH as the proton donor, naphthalene gave the two isomers **a** and **b** (Scheme 2a) in >95% yield. These were obtained in a ratio of **a**/**b** = 1.3. Reduction by the Hilmersson method preferentially yields **b**.[13] The reduction of diphenylacetylene yielded *cis* and *trans* stilbene (Scheme 2b). The overall yield was 90% and the *cis* isomer was obtained, probably as a result of the irradiation of the *trans* isomer. The product from methylbenzoate was benzyl alcohol (80% yield; Scheme 2c).

The photostimulated reactions were performed at high optical density (OD), since under these conditions all of the light is absorbed and the concentration of the reactive reductant (excited SmI_2) is independent of the total concentration of SmI_2. Therefore, as demonstrated in Figure 2, which shows the kinetics for the naphthalene reduction, the reactions were zero order in SmI_2.

A plot of the pseudo-first-order rate constants versus the concentration of naphthalene (Figure 3 and Figures S1 and S2 in the Supporting Information) show that increasing the concentration of the substrate causes a rate increase, which levels off at high substrate concentrations.

The rate as a function of MeOH concentration shows an increase to a maximum at around 1.5 M MeOH followed by a moderate decrease. This is exemplified in Figure 4 for naphthalene and in Figures S3 and S4 in the Supporting Information for the other substrates. These results are consistent with the mechanism shown in Scheme 3.

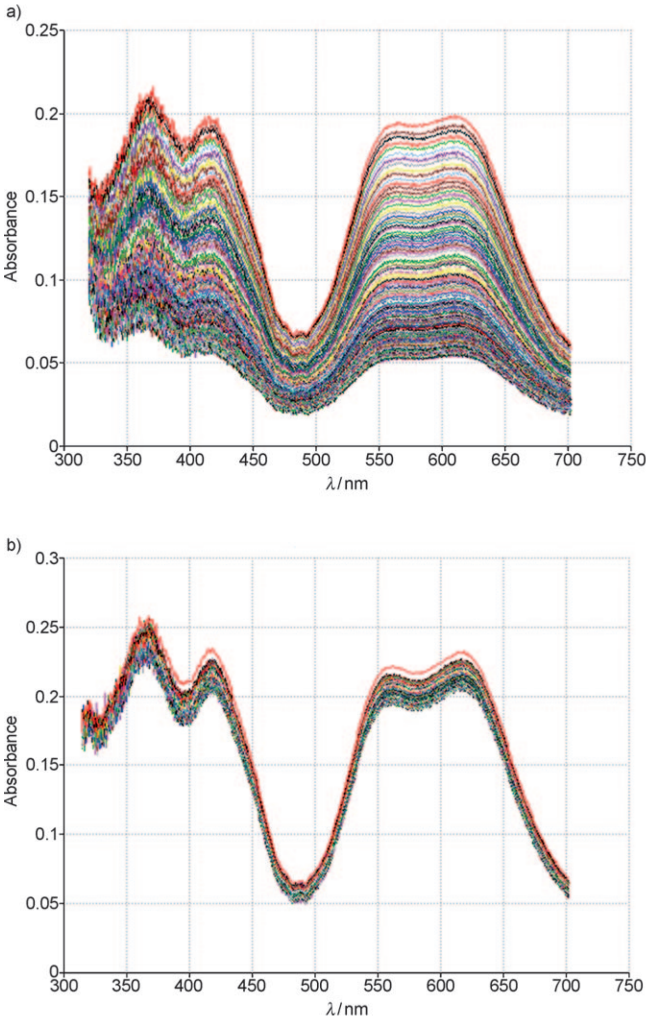
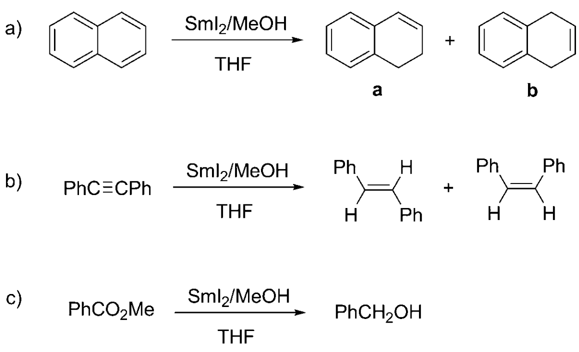


Figure 1. Diode array monitoring of the reaction of naphthalene (0.2 M) and SmI_2 (2.5 mM) in the presence of a) MeOH (1 M, 200 s) and b) TFE (1 M, 800 s).



Scheme 2. Photostimulated SmI_2 reductions.

In the first step, excited SmI_2 may either transfer an electron to the substrate or decay to its ground state. The proba-

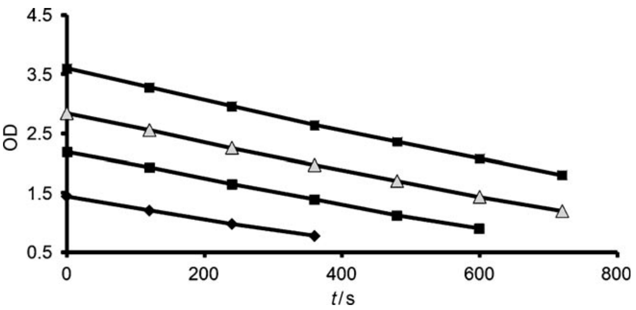


Figure 2. Change of absorption as a function of the irradiation time in the reaction of naphthalene (0.2 M) and 2.17 (◆), 3.28 (■), 4.28 (△), or 5.4 mM (■) of SmI_2 in the presence of MeOH (1 M).

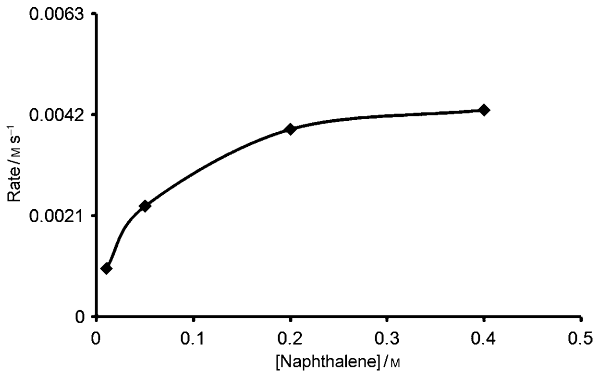


Figure 3. Rate versus naphthalene concentration in its reaction with SmI_2 (4.7 mM) and MeOH (1 M).

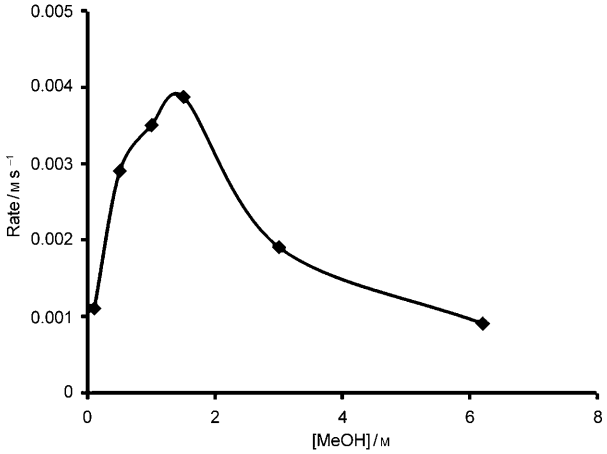
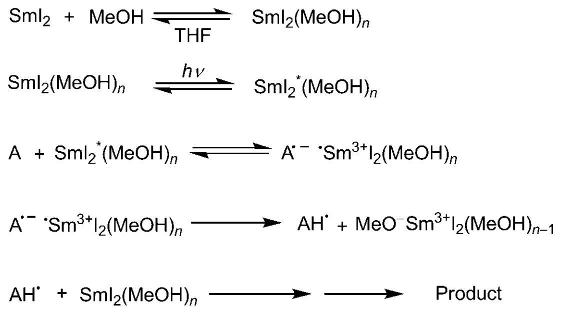


Figure 4. Rate versus MeOH concentration in the reduction of naphthalene (0.2 M) with SmI_2 (5 mM).

bility for electron transfer increases linearly with the concentration of the substrate. The plateau is achieved when all of the excited SmI_2 interacts with the substrate at a rate faster than it decays.[14] Once the radical anion of the substrate is formed it may be protonated by the complexed MeOH, which prevents back electron transfer.

The rate dependence on MeOH is less straightforward. It is expected that the rate will increase as the concentration of MeOH increases. However, if, as we assume, the proton is transferred from MeOH coordinated to the SmI_2, then once the coordination sphere is fully occupied with MeOH molecules, a plateau should be reached. However, the plots for the three substrates show maxima, which are then followed by a decrease in rate. The rate attenuation by MeOH in concentrations over 1.5 M can be explained in two ways. The first explanation is that the electron transfer in our reactions is of the inner-sphere type.[13,15] A tight methanol solvation shell around SmI_2 hinders inner-sphere electron transfer and the reactions at high MeOH concentrations may either take place with the small number of SmI_2 molecules that have an incomplete methanol coordination shell; or the outer-sphere mechanism can also operate, but at a rate lower than that of the inner-sphere mechanism. Alternatively, Scaiano and co-workers reported that the lifetime of SmI_2 in the excited state at 355 nm is lowered,[16] by coordinating HMPA, molecules from 125 to 16 ns in the presence of HMPA (29 mM). It is possible that MeOH coordination has a similar effect on the lifetime of the SmI_2 in the excited state in the visible range. This possibility was tested in the following way: If indeed the lifetime of the excited SmI_2 is shortened by MeOH coordination, then at high MeOH concentration more substrate would be needed to trap the short-lived SmI_2 before it spontaneously decays. As a result, the plateau in the plot of the rate versus substrate concentration would be reached at a higher substrate concentration. We have examined this hypothesis by plotting the rates of the reactions of SmI_2 with naphthalene versus the naphthalene concentration in the presence of 1 and 6.2 M MeOH (Figure 5).



Scheme 3. Photostimulated reactions in the presence of SmI_2 coordinated with proton donors (A = substrate).

The results show that the plateau is reached at about the same concentration of naphthalene and, therefore, we conclude that the reason for the rate decline observed at MeOH concentrations greater than one is due to the hindered approach of the substrate to the MeOH-engulfed excited SmI_2. This inner–outer sphere argument could be refined further. The maximum in the plot of rate versus substrate concentration is around 1.5 M MeOH. However, this concentration is well below the saturation concentration in which the SmI_2 is fully coordinated to methanol molecules. This is evidenced from the spectrum of SmI_2 as a function of MeOH (Figure S5 in the Supporting Information). The

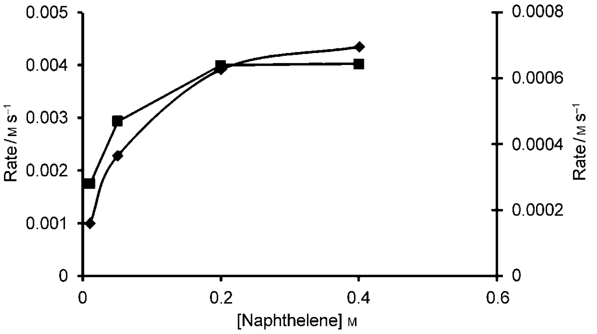


Figure 5. Rate versus naphthalene concentration in its reaction with SmI_2 (4.7 mM) in the presence of 1 (◆) and 6.2 M (■)MeOH, left and right axes, respectively.

double-humped spectrum (560 and 618 nm) typical of SmI_2 in THF coalesces into a single absorption only at MeOH concentrations of around 4 M. Thus, at 1.5 M MeOH, not all the sites around the SmI_2 are taken by methanol molecules and the substrate can form an intimate contact with the SmI_2. Yet, in spite of this incomplete solvation shell, the reaction rate drops. A possible explanation is that there are (at least) two different coordination sites around the SmI_2 and inner-sphere electron transfer occurs preferentially from one of these sites. At MeOH concentrations higher than 1.5 M, MeOH molecules start to occupy this site as well, obstructing the inner-sphere electron transfer and decreasing the reduction rate.

To identify the rate-determining step, we measured the kinetic H/D isotope effect. Table 1 displays the isotope effect as a function of MeOH concentration for the reduction of naphthalene.

Table 1. H/D isotope effect as a function of methanol concentration in the reaction of naphthalene (0.2 M) and SmI_2 (5 mM).

[MeOH(D)] [M]	$Rate_H/Rate_D$
0.1	1.47±0.18
1	1.22±0.29
6.2	1.1±0.2

The isotope effect decreases with the increase in the concentration of MeOH, suggesting that at the beginning protonation is rate determining. However, as the MeOH concentration is increased and there are more MeOH molecules around the SmI_2, the capture of the radical anion by a MeOH molecule from within the ion pair is almost complete and, therefore, proton transfer ceases to be rate determining[17] and the isotope effect decreases.

In conclusion, photostimulated SmI_2 reduction reactions enjoy three major benefits: 1) The reducing power of SmI_2 is significantly increased; more than by any additive. 2) The reaction mixture is not contaminated by an additive. 3) Most substrates are inert to photostimulation at 600 nm. Up to now, and in spite of these advantages, only a very small group of substrates could be reduced this way. We have shown that the applicability range of photostimulated SmI_2 reactions could be vastly extended by converting the bimolecular protonation step to a unimolecular one. It should be noted that ethylene glycol and water also form strong complexes with SmI_2 and may serve the same purpose as MeOH.[18] This effectively prevents the rapid back electron transfer, which was found to be the cause for the limited applicability of photostimulated SmI_2 reductions. Thus, we demonstrate once again the importance of understanding the mechanistic details of a reaction to design a successful strategy for its employment.

Keywords: electron transfer · photochemistry · radical ions · reduction · samarium iodide

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[17] Depending on the concentration of the substrate, the rate-limiting step may be either the electron transfer or the rate may be independent of any of the reactants and be affected only by the irradiation intensity.

[18] We chose MeOH because its reaction rates were more suitable for our measurements.

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