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Synergism and Inhibition in the Combination of Visible Light and HMPA in SmI_2 Reductions

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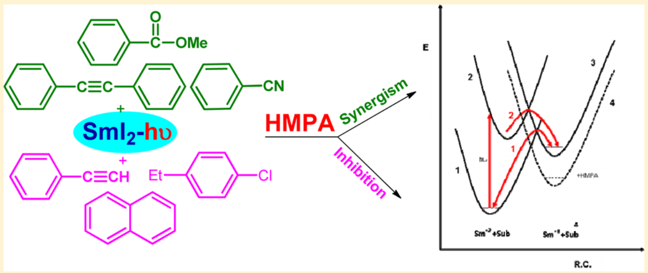
S Supporting Information



ABSTRACT: The reaction of six substrates (diphenylacetylene, benzonitrile, methyl benzoate, phenylacetylene, naphthalene, and 1-chloro-4-ethylbenzene) with SmI_2 in the presence of MeOH or TFE was studied. The reactions were monitored under three different conditions: (a) irradiation, (b) irradiation in the presence of HMPA, and (c) reactions in the presence of HMPA in the dark. The combination of visible light and HMPA was found in some cases to be synergistic, in others to be additive, and in four cases to be inhibitive. The Marcus theory provides a good understanding of the synergistic and the additivity phenomena. The inhibitive effect is traced to the post electron transfer step in which Sm^{3+} plays an important role. Once coordinated to HMPA, Sm^{3+} is less capable of assisting in the protonation of the radical anion or the expulsion of the leaving group. Ranking according to the substrate's electron affinity shows that inhibition is manifested for the three least electrophilic substrates: phenylacetylene, naphthalene, and 1-chloro-4-ethylbenzene. Typical of these substrates is the short lifetime of their radical anions. Thus, if a step consecutive to electron transfer is slow and cannot compete successfully with the rapid back electron transfer, the benefit of having the electron transfer step enhanced is much reduced.

■ INTRODUCTION

The reduction potential of SmI_2, which is a very useful one-electron transfer reducing agent,[1] can be boosted in one of two ways: either by appropriate ligation—a popular ligand is HMPA[2]—or by irradiation in the 580–620 nm range.[3,4] This paper focuses on the question of whether these two factors are additive or not. As will be shown, in certain cases, the combination of the two is even synergistic, while in others not only is it not additive but is in fact also counterproductive.

It is clear that the enhancement by the electronic excitation of SmI_2 is caused by raising the energy of an electron in its outer shell. In addition, ligation may affect the lifetime of the excited state.[5] Whether the combination of light and HMPA is additive or not depends, among other things, on the origin of the HMPA effect on the reduction potential of SmI_2. The HMPA effect might be caused either by raising the energy level of the HOMO or by stabilization of the product Sm^{3+}. If the HMPA effect is caused by raising the HOMO energy, assuming that the energy of the LUMO is unchanged, the addition of HMPA to a photocatalyzed reaction will not change the rate of the reaction, since the electron after excitation will still be in a LUMO of the same energy as before. On the other hand, if the effect stems from stabilization of Sm^{3+}, the two-intersecting-parabolas model dictates an increase in the rate of the electron transfer in the photocatalyzed reaction as a result of the addition of HMPA. In a previous work we have shown[6] that, at least in part, the HMPA effect stems from stabilization of the product—Sm^{3+}. This was done as follows: the addition of HMPA to a SmI_2 solution causes the two humps in the VIS spectrum of SmI_2 at 580 and 619 nm to merge into a slightly blue shifted single peak. The addition of an equivalent amount of Sm^{3+} (as SmI_3) to the solution completely regenerated the original double-humped spectrum of SmI_2.

■ RESULTS AND DISCUSSION

Figure 1 shows the substrates that were examined in this study.

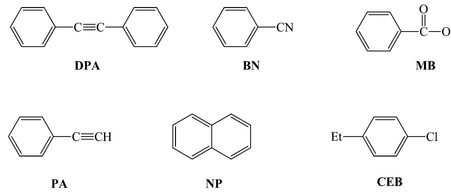


Figure 1. Substrates studied in this work.

All the reactions were performed in three different modes: (a) irradiation without HMPA, (b) irradiation with HMPA, and (c) reactions performed in the presence of HMPA in the dark. All substrates were reacted in the presence of methanol. Several reactions were performed also in the presence of trifluoroethanol (TFE). The major difference between the two alcohols, relevant to this study, is their ability to form complexes with SmI_2.[7] While methanol forms complexes with SmI_2, TFE fails to do so. We have shown in the past[4,8] that

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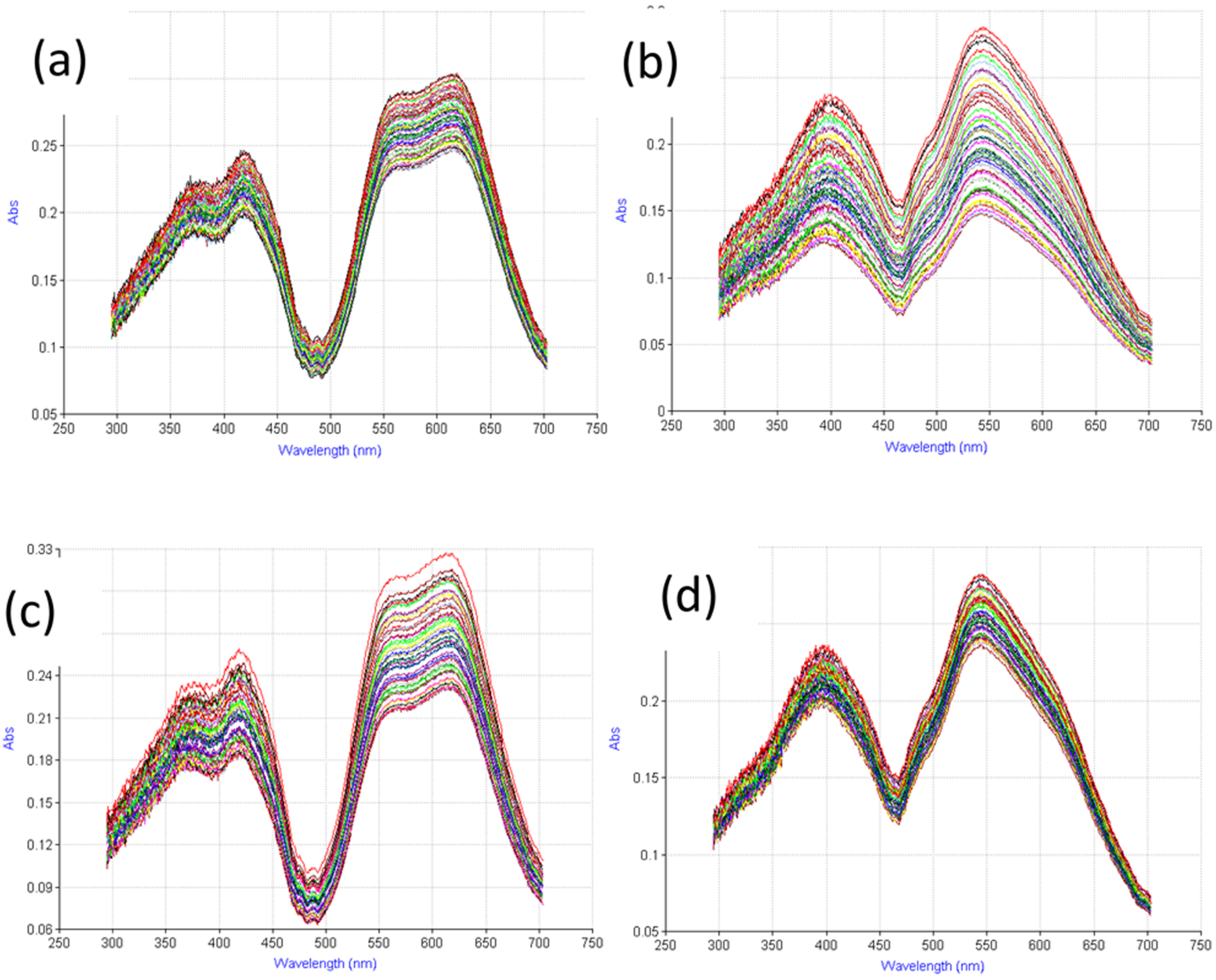

Figure 2. Diode array irradiation and monitoring of the reaction of SmI_2: (a) with BN(MeOH)−light; (b) with BN(MeOH)−light and HMPA (positive combination); (c) with CEB(MeOH)−light; (d) with CEB(MeOH)−light and HMPA (negative combination).

substrates having a short-lived radical anion (DPA, NP, and BN) will not yield the product if the proton donor is not present in the vicinity of the radical anion: namely, complexed to the SmI_2. In such a case, the electron will bounce back from the radical anion to the Sm^{3+} before the bimolecular protonation by a proton donor from the bulk solution will trap the radical anion. Therefore, the reactions of DPA, NP, and BN in the presence of TFE were not investigated. Except for the slowly reacting substrates DPA, BN, and NP, whose concentrations were 0.1 M, the substrate concentration was 0.01 M. The concentration of the proton donor was 0.2 M, the SmI_2 concentration was 0.005 M, and that of HMPA, when present in the reaction, was 0.16 M. The reactions were performed in the stopped-flow spectrophotometer using the diode array mode. In this mode the sample is irradiated for long periods of time, enabling simultaneous monitoring of the progress of the reaction.[4] An example of monitoring of the photocatalyzed reaction using the diode array is given in Figure 2. The remainder of the results are presented in the Supporting Information.

Given in Table 1 are the decreases in the SmI_2 absorptions at 619 nm observed in the three modes of reaction: photocatalyzed reaction, photocatalyzed reaction combined with HMPA, and reaction with HMPA in the dark. The decrease in the optical density is proportional to the extent of the reaction at the noted reaction times. It should be pointed out that the study was not aimed at the determination of rate constants but rather was intended to get a semiquantitative measure of the extent and efficiency of the reaction. Therefore, in most cases the reactions were not performed under pseudo-first-order conditions. A comparison between the ΔOD(HMPA) and that of the combination of light and HMPA (ΔOD($h\nu$+HMPA)) shows, as expected, that in no case does light reduce the activity of the HMPA. On the other hand, a comparison between the photocatalyzed reaction itself and its combination with HMPA shows that in five cases the combination effect is larger than that of the photocatalysis reaction and in four cases that HMPA hampers the efficiency of the photocatalyzed reaction. For the substrate PA(MeOH) the combination effect is rather negligible. A convenient indicator for the efficiency of the combination is the ratio ΔOD($h\nu$+HMPA)/[ΔOD(HMPA) + ΔOD($h\nu$)]. In the reactions where the combination of the two factors, $h\nu$ and HMPA, leads to a synergistic effect (the sum total is larger than that of the algebraic sum of the individual

Table 1. Extent of Reaction Progress for Reactions Carried out in Three Modes, Photocatalyzed Reaction, Photocatalyzed Reaction in the Presence of HMPA, and the Reaction of HMPA in the Dark, and the Combination Efficiencies[a]

	time (s)	ΔOD($h\nu$)	ΔOD($h\nu$+HMPA)	ΔOD(HMPA)	efficiency
DPA (MeOH)	50	0.030	0.090	0.048	1.15
	100	0.041	0.133	0.061	1.30
BN (MeOH)	10	0.057	0.141	0.028	1.66
	50	0.148	0.232	0.053	1.15
MB (MeOH)	5	0.035	0.097	0.065	0.97
	10	0.048	0.156	0.086	1.16
MB (TFE)	5	0.022	0.168	0.054	2.21
	10	0.026	0.200	0.107	1.50
PA (MeOH)	50	0.070	0.058	0.039	0.53
	100	0.097	0.108	0.051	0.73
PA (TFE)	50	0.021	0.075	0.06	0.93
	100	0.031	0.143	0.048	1.81
NP (MeOH)	50	0.108	0.030	0.013	0.25
	100	0.143	0.046	0.021	0.28
CEB (MeOH)	10	0.059	0.031	0.026	0.36
	20	0.098	0.049	0.049	0.33
CEB (TFE)	10	0.062	0.046	0.029	0.51
	20	0.089	0.069	0.027	0.59

[a] The reactant concentrations were [ROH] 0.2 M, [SmI_2] 0.005 M, and [HMPA] 0.16 M. The substrate concentration was 0.01 M, except for DPA and BN, where it was 0.1 M.

contributions), this ratio will be higher than 1. Values around unity indicate the algebraic additivity of the two rate-enhancing components. In reactions where the combination of the two is counterproductive (HMPA slows down the photocatalyzed reaction), this ratio will be significantly lower than unity. The trends presented at Table 1 were confirmed by performing many repetitions at different times and at different concentrations.

One of the most interesting phenomena encountered in this study was that for BN the efficiency was dependent on the concentration of the substrate. For example, for a concentration of 0.01 M (all other concentrations were the same as in Table 1), it was found that after 50 s the efficiency was 0.43, and after 100 s, it was 0.38 (see the Supporting Information). Thus, at the high (0.1 M) BN concentration, the combination of light and HMPA is synergistic (efficiency greater than 1), while at the low BN concentration (0.01 M) the effect of HMPA on the photocatalyzed reaction is negative and the efficiency factor is 0.45. This dependence on the substrate concentration stems most probably from the benzalamine produced in this reaction. This product apparently has a negative combination effect. At a low BN concentration, the generated benzalamine competes effectively with the BN for the SmI_2 and therefore decreases the enhancing effect of the combination.[9] At high BN concentration the benzalamine cannot compete so effectively with the substrate, which is present in a large excess, and therefore the outcome is much more positive. This is consistent with the decrease in the efficiency (Table 1) from 1.66 to 1.15 upon going from 10 to 50 s reaction time. As the reaction progresses, the concentration of benzalamine increases. After 50 s there is more benzalamine produced than after 10 s, and therefore, it affects the outcome of the combination efficiency to a larger extent.

In addition to the diode array experiments we have also performed two series of preparative reactions: one series for the substrate BN, which manifested a positive combination of light and HMPA, and another series for CEB,[10] for which the effect of this combination was negative. The preparative reactions were performed in a Pyrex flask using a 500 W incandescent lamp, according to the procedure previously published.[8] Yields were determined by NMR. Shown in Figure 3 are the results of the preparative reaction of BN conducted under the following conditions: irradiation time 5 min, reactant concentrations [BN] = 0.02 M, [SmI_2] = 0.04 M, and [MeOH] = 0.2 M (see the Supporting Information).[11] The figure clearly shows that as the concentration of HMPA increases the yield increases, as does the yield of the photocatalyzed reaction. Namely, the combination of light and HMPA is positive, as in the reactions performed using the diode array method.

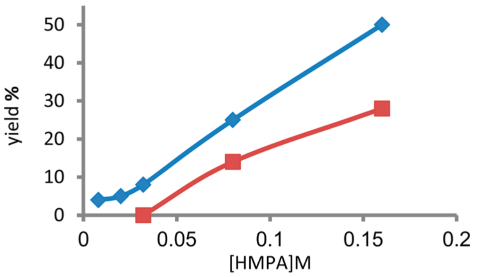

Figure 3. Effect of HMPA concentration on the yield of the reaction of BN (brown line) and its effect on the photocatalyzed reaction (blue line).

In contradistinction to BN, with CEB, there is no dark reaction with HMPA, and in 1 h irradiation time, using concentrations [CEB] = 0.02 M and [SmI_2] = 0.04 M, the following yields of ethylbenzene as a function of the HMPA concentration were obtained: in the absence of HMPA, 20%; in the presence of 0.04, 0.08, and 0.16 M HMPA 19, 8, and 6%, respectively. Thus, the preparative reaction using the incandescent lamp confirmed the diode array results showing that HMPA significantly lowered the efficiency of the photocatalyzed reaction.

Let us now discuss the theoretical aspect of the phenomena. In Figure 4, parabola 1 is the reactants' ground state, parabola 2

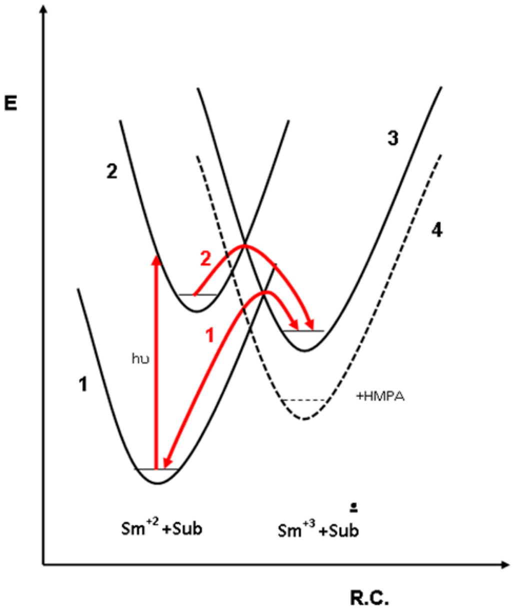

Figure 4. Parabola model of ground state and excited state for electron transfer reaction between a substrate (Sub) and Sm^{2+}.

represents the excited state, and parabola 3 represents the ground state of the products, namely the ion pair consisting of the radical anion of the substrate and Sm^{3+}.

In the thermal reaction the electron moves from parabola 1 to parabola 3 (arrow 1 from left to right) over the barrier located in the vicinity of their crossing point (avoided crossing zone). At this point there could be a reversal of the electron transfer (motion from right to left along arrow 1) or continuation to the following step, not shown in the figure. This step could be protonation, dissociation, or any other process which the radical anion may undergo. In order for the reaction to occur, this step must compete successfully with the facile return of the electron to the ground state. HMPA probably affects the stability (height) of all the parabolas, but its dominant effect will, most probably, be on parabola 3, shifting it into parabola 4.[12] This stabilization of Sm^{3+} by HMPA has two effects that enhance the reaction. The first is the reduction of the barrier height for the transfer of the electron from the Sm^{2+} to the substrate. The second is the increase of the barrier height for the return of the electron to the starting material. The second effect is of special importance in cases where the consecutive reaction that the radical anion undergoes is rate determining, since it increases the lifetime of the radical anion and enables its efficient trapping before the system gravitates back to the ground state of the starting material.

In the photocatalyzed reaction, excitation yields an excited Sm^{2+} with the substrate at its ground state (parabola 2) and apparently, after thermal decay to the vibrational ground state of this electronically excited state, an electron transfer to parabola 3 occurs (arrow 2). Here too, the stabilization of Sm^{3+} by HMPA will reduce the barrier for the electron transfer from the excited state to the substrate, increasing the efficiency of the electron transfer relative to the radiationless decay of the excited state. In addition, as discussed above, it increases the probability of the consecutive reaction to occur by slowing the back electron transfer process (arrow 1 from right to left). Thus, in principle the HMPA should also have a positive effect on the photocatalyzed reactions, as it has in the non-photocatalyzed reaction.

The synergistic effect (efficiency >1) is observed most likely due to different curvatures of the different parabolas (namely, the crossing point will be achieved at a lower energy). By the same token, efficiency slightly smaller than 1 may still indicate a positive collaboration of the two contributors, although, due to variation in curvature, not an algebraic one.

In light of the aforementioned discussion, the question to be answered is why the addition of HMPA to the photocatalyzed reactions of CEB (MeOH and TFE), NP (MeOH), and PA (MeOH) slows down the reactions and reduces their efficiency. Ab initio calculations[13] at the B3LYP/6-31+G* level of the neutral substrates and their radical anions yield the adiabatic electron affinity[14] shown in Table 2 (geometries and energies are given in the Supporting Information).

Table 2. Calculated Electron Affinity (EA) of the Substrates in the Gas Phase

substrate	EA (kcal/mol)	substrate	EA (kcal/mol)
MB	−13.69	PA	5.52
DPA	−7.30	NP	6.00
BN	−2.17	CEB	21.00

The three molecules that manifest the counterproductive effect in the combination of HMPA and light are shown to be the least electrophilic molecules in this series. It should be pointed out that an upward vertical shift of parabolas 3 and 4 relative to 2, mimicking a more endothermic electron transfer process to these substrates, will cause an overall rate retardation but not a negative effect of HMPA on the photocatalyzed reaction. The rate retardation caused by HMPA on the photocatalyzed reactions in these cases could originate from several sources. For obvious reasons, the least probable origin is that these systems with HMPA have reached the Marcus inverted region.[15] Although it is theoretically sound, there are only very few claims for the observation of the inverted region and, in addition, its existence is highly debatable.[16] Another possible cause for this negative effect within the Marcus theory is the physical separation of Sm^{2+} from the substrate due to the HMPA coordination shell. This separation of the reactants is inhibiting because it decreases the tunneling element which is strongly dependent on the distance separating the two reacting centers.[16] However, the fact that this factor is common for all the substrates makes it clear that this is not the cause for the negative HMPA effect observed. In other words, this separation should have affected all substrates to a similar extent and not only the substrates of low electron affinity. We believe that the reason for the negative effect stems from the lifetime of the radical anions. A major consequence of the low electrophilicity of PA, NP, and CEB is the short lifetime of their radical anions. This lifetime, which determines the efficiency of the reduction reaction, is governed by the height of the barrier for the back transfer of the electron (motion along arrow 1 from right to left). The consecutive step, which leads from the radical anion to the product, has to compete successfully with this facile back electron transfer, in order for the reaction to occur. This is why, for example, naphthalene cannot be photoreduced by SmI_2 using TFE as a proton donor.[4] This proton donor, which does not form complexes with SmI_2, protonates the radical anion in a bimolecular fashion. Thus, if the lifetime of the radical anion is short, the probability of an encounter with the proton donor molecule from the bulk solution is significantly reduced. The protonation of the radical anion by a methanol molecule complexed to the Sm^{3+} within the ion pair is a unimolecular process which renders an otherwise impossible reaction into a possible one, as we have shown for both ground-state[17] and photocatalyzed reactions.[4]

The added HMPA slows down the rate of the back electron transfer; therefore, it lengthens the lifetime of the radical anion.[18] However, if it slows down the consecutive step more than it slows down the back electron transfer, the net outcome will be a significant rate retardation of the reaction. For NP (MeOH) and PA (MeOH), we have shown earlier that the step which traps the radical anion before it transfers the electron back to Sm^{3+} is protonation by a methanol molecule complexed to the Sm^{3+} within the ion pair. The addition of HMPA, which efficiently complexes to SmI_2, reduces the ability of methanol molecules to complex with the SmI_2 and may also distance the fewer MeOH molecules which are complexed to the Sm^{3+} from the radical anion. This of course will lower the competitiveness of the internal protonation with respect to the back electron transfer process and therefore will cause a negative HMPA effect on the combination. In the case of CEB, where no protonation is needed before the rate-determining step, most probably, the expulsion of the chloride from the radical anion must be assisted by the Sm^{3+} ion. Again, it is highly likely that the complexation of Sm^{3+} by HMPA reduces the ability of Sm^{3+} to assist in this expulsion and therefore HMPA will cause retardation of the rate-determining step. This in turn, will enable the back electron transfer from the radical anion of CEB to Sm^{3+} to occur, inhibiting the photocatalyzed reaction and resulting in low efficiency values.

■ SUMMARY AND CONCLUSIONS

In this work we have examined the possibility of combining two popular methods to increase the reduction ability of SmI_2: ligation by HMPA and irradiation in the visible region. It turned out that there are three possible outcomes of this combination. The first is a synergistic effect: namely, the rate enhancement of the combination is larger than the algebraic sum of the individual contributors (HMPA and light). The second is when the result is greater than the effect of each of the individual contributors but not synergistic. The third is when the effect of added HMPA is negative: namely, it hampers the efficiency of the photocatalyzed reaction.

Addition of HMPA enhances the rate of the electron transfer by stabilizing the product (Sm^{3+}) more than the reactant (Sm^{2+}). This applies both to the thermal and to the photochemical reaction. Moreover, the crossing-parabolas model shows that it also raises the barrier for the back electron transfer to the ground state of the starting material. Thus, in principle, the effect of HMPA should be overall positive. Yet as we have shown, in certain cases it has a negative effect. The cases where its effect was negative feature low electrophilicity of the substrate: that is to say, a short lifetime of the radical anion. In these reactions, due to the short lifetime of the radical anion, it is essential to have the Sm^{3+} in the vicinity of the radical anion for the successive step to occur. In the case of PA and NP, protonation of the radical anion by MeOH complexed to the Sm^{3+} is the successive step. In the case of CEB it is the assistance to the departure of the chloride ion. In both cases, the complexation by HMPA is counterproductive and therefore the efficiency of the photocatalyzed reaction is diminished by HMPA. In cases where the lifetime of the radical anion is long enough, this effect plays a much smaller role.

It is therefore concluded that the combination of light and HMPA is beneficial only with substrates of sufficiently high electron affinity. On the other hand, substrates of low electrophilicity in which the consecutive rate-determining step necessitates the presence of Sm^{3+} in the close vicinity of the radical anion will suffer reduction in the efficiency of the photocatalyzed reaction due to the addition of HMPA.

■ EXPERIMENTAL SECTION

General Considerations. THF was dried over Na wire, in the presence of benzophenone, and distilled under an argon atmosphere. The freshly distilled THF was used for all reactions. TFE, MeOH, and HMPA were dried according to known procedures.[19] SmI_2 solutions of 0.1 M in THF were prepared according to a published procedure[20] and diluted as needed. The concentration of the SmI_2 solutions was spectroscopically determined (λ 619 nm; ε = 635 M^{-1} cm^{-1}). Commercial benzonitrile, 1-chloro-4-ethylbenzene, methyl benzoate, and phenylacetylene were distilled. Naphthalene and diphenylacetylene were recrystallized prior to use.

Diode Array Experiments. The progression of the reaction was monitored using the diode array mode of a stopped-flow spectrophotometer. The decrease in optical density (OD) is proportional to the extent of the reaction at the noted reaction times. The following concentrations were used for the light as well as the dark reactions: substrate (0.01 or 0.1 M), methanol or TFE (0.2 M), SmI_2 (0.005 M), HMPA (0.16 M). The substrate and the proton donor were placed in one syringe and the SmI_2 (or SmI_2–HMPA) in another.

Preparative Reaction. Reductions of benzonitrile or 1-chloro-4-ethylbenzene under light, light–HMPA, and HMPA–dark were conducted as follows: a freshly prepared solution of SmI_2 (0.04 M) in THF was added in a glovebox to a homogeneous solution of substrate, benzonitrile or 1-chloro-4-ethylbenzene (0.02 M) containing MeOH (0.2 M), and HMPA (concentrations ranged from 0.004 to 0.16 M) in dry THF. The total volume of the reaction mixture was 25 mL. The volumetric flasks were removed from the glovebox and placed next to a 500 W incandescent lamp. During the irradiation, the temperature of the reaction mixture reached 40 °C. The reactions were stopped after a given time, and the excess SmI_2 was quenched with iodine. The reaction mixture was diluted to 50 mL with diethyl ether in a separatory funnel, washed with 15% aqueous KOH solution for benzonitrile and 5% aqueous phosphate buffer solution (6 mL) for 1-chloro-4-ethylbenzene and then with brine solution (20 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure at 25 °C. The crude reaction mass was analyzed. The yields of benzylamine[8,21] and ethylbenzene[22] were determined by ^1H (300 MHz) and ^{13}C NMR (75 MHz) and are based on SmI_2 consumption.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and text giving diode array spectra, preparative reaction data, the complete ref 13, and energies and geometries of the QM calculated substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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