

Communication between Surfaces by Electron Relay in a Doubly Heterogeneous Photochemical Reaction

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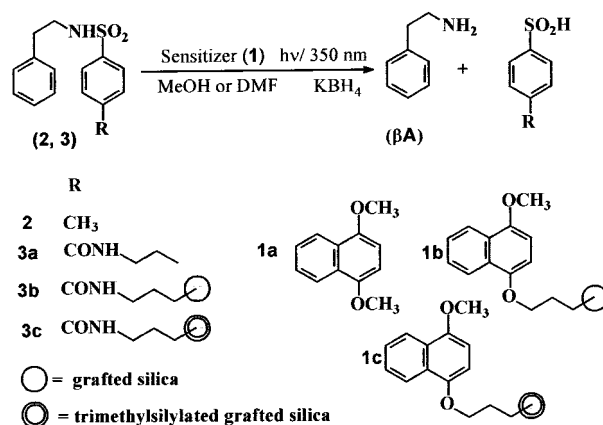
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Photochemical reactions using sensitizers covalently linked to the surface of silica beads have already been reported.^{1–6} Supported photosensitizers used as a suspension in a liquid offer obvious advantages: ease of photoproducts separation, analysis simplification, recycling of the sensitizer, and circumventing a poor solubility in the reaction medium are among these benefits. In addition to those obvious advantages, it has been shown that the organization of sensitizers on the silica surface plays an important role.⁶

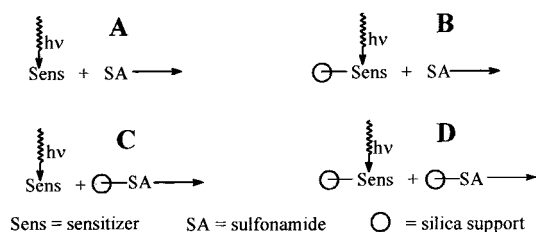
In this paper, we show that the surface of organically modified silica beads may be photoactivated using a sensitizer in the solution together with an electron relay: an amine is unhooked from a sulfonamide substrate attached to the silica. Furthermore it was found that a doubly heterogeneous sensitized system in which the sensitizer and the sulfonamide substrate are attached to different silica beads works even better: an electron relaying shuttle ensures communication between the beads. This “synaptic like” system, which has not been explored as yet, opens the way to new kinds of photochemical processes or investigations. This surface to surface communication is, to our knowledge, the first example of a photoinduced electron transfer organic reaction photosensitized on one surface and relayed to another one. A nonphotochemical system related to our work may however be cited: an alcohol was shown to be alternately reduced and oxidized on the surfaces of silica and alumina beads charged with appropriate redox reagents.⁷

In this paper the photoreductive deprotection of sulfonamides^{8,9} is taken as a test reaction for the study of heterogeneous conditions: in our example, 1,4-dimethoxynaphthalene (**1a**) sensitizes the cleavage of the sulfonamides **2** and **3** in the presence of potassium borohydride coreductant. Scheme 1 embodies this photodeprotection from which β -phenethylamine (β A) is recovered together with *p*-toluene sulfonic acid. The first step of the mechanism is without doubt a photoinduced electron transfer (PET) reaction from the excited sensitizer toward the accepting sulfonamide: the fluorescence of excited **1a** is quenched by **2** or **3a** with Stern–Volmer constants (= product of quenching rate constant by the **1a*** lifetime) of 19 and 71 M⁻¹, respectively. The difference between the two values is due to the better electron accepting character of **3a**. The exact role played by the hydride is almost unknown: it is unable to perform the cleavage of the

Scheme 1



Scheme 2



sulfonamide by itself and, on the other hand, the photochemical reaction is very inefficient in its absence. The hydride is probably involved in the sensitizer regeneration and a salt effect helping ion pair separation is also possible.

Four different experimental systems (Scheme 2) were used: homogeneous reaction (system **A**), heterogeneous system with sensitizer (system **B**) or substrate (system **C**) covalently grafted on silica, and the doubly heterogeneous system with sensitizer and substrate grafted on different silica beads (system **D**). (See Table 1 for results.)

That the homogeneous method (**A**) allows a complete deprotection with a 100% transformation into amine and sulfonic acid can be seen in runs 1 and 3. The sulfonamide group is selectively cleaved while the amide function of **3a** remains unaffected: the concentration of recovered amine correctly matches the sulfonamide consumption.

If the sensitizer concentration is raised above 1.5×10^{-4} M, the situation rapidly deteriorates: the sensitizer is consumed and secondary products are found, explaining bad yields such as in run 2. The secondary reactions were found to involve excited and ground state **1a**. By fixing the sensitizer on a surface these reactions are suppressed. Runs 6 and 7 (system **B**) show that the reaction works, even if slower (compare runs 1 and 6 using **2** as substrate). The fluorescence quenching of **1b** by **3a** has been measured with a Stern–Volmer constant of 14 M⁻¹ showing a decrease of reactivity when going to the heterogeneous system **B**. However, in this system and as shown in run 8, the sensitizer concentration limit is no longer operative as a benefit of using an immobilized sensitizer. In this run, the sensitizer has been filtered, washed, and successfully recycled: the efficiency of the grafted sensitizer remained unchanged. According to the estimation of the **1b** silica loading, a turnover of the sensitizer of 80 is found as a minimum.

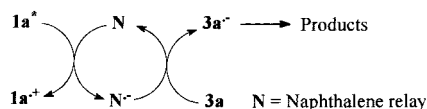
The sulfonamide substrate has been attached to the surface of a silica and used in system **C**. Run 9 again shows the adverse effect of an increase of **1a** concentration in solution, with a large amount of consumed sensitizer. In run 10, traces of products are

- (1) Horner, L.; Klaus, J. *Justus Liebigs Ann. Chem.* **1981**, 792–810.
- (2) Avnir, D.; Wellner, E.; Ottolenghi, M. *J. Am. Chem. Soc.* **1989**, *111*, 2001–2003.
- (3) Julliard, M.; Legris, M.; Chanon, M. *J. Photochem. Photobiol. A: Chem.* **1991**, *61*, 137–152.
- (4) Julliard, M.; Chanon, M. *Bull. Soc. Chim. France* **1992**, *129*, 242–246.
- (5) Julliard, M. *New J. Chem.* **1994**, *18*, 243–250.
- (6) (a) Ayadim, M.; Soumilion, J. Ph. *Tetrahedron Lett.* **1995**, *36*, 4615–4618 (b) Ayadim, M.; Soumilion, J. Ph. *Tetrahedron Lett.* **1996**, *37*, 381–384.
- (7) Kim, B.; Regen, S. L. *Tetrahedron Lett.* **1983**, *24*, 689–690.
- (8) Umezawa, B.; Sawaki, S.; Oshino, O. *Chem. Pharm. Bull.* **1970**, *18*, 182–185.
- (9) Hamada, T.; Nishida, A.; Yonemitsu, O. *J. Am. Chem. Soc.* **1986**, *108*, 140–145.

Table 1. Homogeneous and Heterogeneous Photosensitized Cleavage of Sulfonamides^a

run ^b	sens. ^c	time (h)	SA ^{c,d}	relay ^e	amine ^{e,f,g}
1 (A)	1a (0.5)	35	2 (15)	—	15
2 (A)	1a (1.5)	4.5	2 (36)	—	3.0
3 (A)	1a (0.7)	28	3a (50)	—	50.0
4 (A)	1a (0.5)	0.5	3a (30)	—	7.5
5 (A)	1a (0.5)	0.5	3a (30)	+	2.5
6 (B)	1b (0.6)	20	2 (15)	—	1.5
7 (B)	1b (0.6)	28	3a (48)	—	47.0
8 (B)	1b (1.8) ^h	45	3a (50)	—	50.0
9 (C)	1a (14) ⁱ	5.5	3b (31)	—	0.2
10 (C)	1a (0.5)	23	3c (<20)	—	<0.04
11 (C)	1a (0.5)	23	3c (<20)	+	2.5
12 (D)	1b (0.6)	28	3b (31)	—	0
13 (D)	1b (0.6)	28	3b (31)	+	0
14 (D)	1b (0.6)	28	3b (31)	+	0
15 (D)	1c (<0.6)	28	3c (<20)	+	7.3
16 (D)	—	28	3c (<20)	+	0
17 (D)	1c (<0.6)	28	3c (<20)	+	0 ^j
18 (D)	1c (<0.6)	28	3c (<20)	—	0

^a 5 mL reaction mixture irradiated with black light phosphor lamps (350 nm, 12 W, 15 cm from sample). Degassing under argon. Solvent: MeOH in runs 1–3, 6–9, 12, and 13. DMF in other runs. ^b See Scheme 2. ^c μmol in the 5 mL reacting volume. ^d SA = sulfonamide. ^e Naphthalene electron relay; 500 μmol in reacting volume. ^f Recovered β -phenethylamine. ^g In runs 1 and 3–8: 100% recovery of amine versus consumed sulfonamide. In run 2: 30%. ^h Sensitizer successfully reused after this run. ⁱ 66% of sensitizer consumed after reaction. ^j No KBH_4 in this run.

Scheme 3

only obtained and a considerable drop of the reactivity is observed (compare runs 4 and 10). Remembering that a PET reaction needs contact between the reactants, the lifetime of excited **1a** (around 6 ns)¹⁰ is probably not sufficient to allow it to reach the surface bearing the immobilized sulfonamide: the deactivation of the excited state is much faster than its diffusion to the solid particles.

A solution to this particular problem may be a shuttling molecule. This one should accept an electron from excited **1a** and carry it to the substrate anchored to the silica beads. Excited **1a** is quenched by naphthalene (**N**) through a PET process¹⁰ with a Stern–Volmer constant of about 2 M^{-1} . This makes **N** a good candidate for the electron relay, working as shown in Scheme 3 with an anion-radical of sufficient lifetime.

Runs 10 and 11 were performed in a nonprotic solvent and the grafted silica was trimethylsilylated to avoid the destruction

(10) Habib Jiwan, J. L.; Soumillion, J. Ph. J. Phys. Chem. **1995**, *99*, 14223–14230.

of the naphthalene anion-radical. Comparison between these runs shows that the relaying system works and significantly enhances the yield. It is worth mentioning that the homogeneous reaction (system **A**) works better in the absence of the electron relaying **N** (see runs 4 and 5): the reaction yield is lowered by a factor of about 3 in the presence of **N**, and this means that **N** effectively intercepts **1a*** but that the shuttling efficiency is insufficient for maintaining the reaction yields. Efficient electron relay cosensitizations are known^{11,12} and their functioning was analyzed.¹³ It is striking to see that even when not efficient in homogeneous reactions, electron relay systems may be useful in heterogeneous systems.

Experiment 15 clearly shows that a doubly heterogeneous sensitized system may be used (system **D**), with even better results than in system **C**. Of course, all the reaction conditions necessary to keep the **N** radical anion working must be met (runs 12–18): the remaining silanol groups of **1c** and **3c** were removed by trimethylsilylation and the methanol solvent was replaced by DMF. Under those conditions, the obtained deprotection yield was probably only limited by the sulfonamides remaining accessible on the surface of **3c**. Longer irradiation times did not liberate larger amounts of amines and this shows that the available surface sulfonamides of **3c** are completely photocleaved. It is not unreasonable to think that a significant fraction of the grafted sulfonamide may be buried in holes closed by the silylating treatment: we have shown, in another work, that on a highly loaded grafted silica about one-third of the grafted molecules remain accessible.^{6b} The same masking phenomenon may deactivate a fraction of the sensitizer in **1c**. If this is true, our doubly heterogeneous system is still more efficient than expected.

In this reaction, two heterogeneous electron transfers are taking place successively. What is presented here is of interest in systems where a surface needs to be modified by a remote photoactivation as in cases where the sensitizer and the surface are chemically incompatible. In the present work, the surface is not sensitive to the direct action of the sensitizer and is made sensitive to its remote activation by way of a shuttling electron carrier.

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Supporting Information Available: Experimental details, including the synthesis procedures for **1b**, **3a**, and **3b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA990316A

(11) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012–3026.

(12) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663–664.

(13) Vauthey, E.; Pilloud, D.; Haselbach, E.; Suppan, P. *Chem. Phys. Lett.* **1993**, *215*, 264–268.