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Highly Efficient Photoinduced Electron Transfer with 2,4,6-Triphenylpyrylium Cation Incorporated inside Extra Large Pore Zeotype MCM-41

Avelino Corma, Vicente Fornés, Hermenegildo García,* Miguel A. Miranda,* and María J. Sabater

Instituto de Tecnología Química
Universidad Politécnica de Valencia
Apartado 22012, 46071-Valencia, Spain

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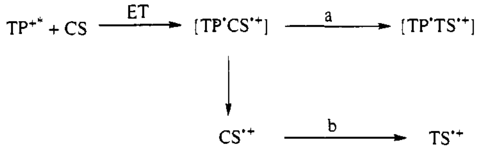
The efficiency of photoinduced electron transfer is generally limited by the occurrence of deactivating back electron transfer, which competes with other reactive pathways of the generated radical ion pairs.[1] Different methodologies are being pursued to minimize this undesired process. Thus, laser flash photolysis techniques have shown that medium- and large-pore zeolites provide an appropriate microenvironment for this purpose, retarding dramatically the back electron transfer and increasing enormously the lifetime of the photogenerated ion pair.[2] This fact has been ascribed to the strong electrostatic fields experienced inside the voids of these solids, which must produce a high stabilization of the radical ions. In spite of these highly promising results, the above findings have not yet been exploited to increase the efficiency of photoinduced electron transfer processes from a preparative point of view.

In heterogeneous reactions using microporous systems, impeded diffusion of the reagents and accessibility of the sites are limiting factors of paramount importance. In fact, the relatively small size of the micropores (typically ≤1.3 nm) has been claimed as the main drawback for an intensive use of zeolites as microscopic reactors.[3] Therefore, it is interesting to determine the suitability of new zeotypes with extra large pore dimensions as hosts to perform photoinduced electron transfer reactions with bulky photosensitizers or substrates. Much effort is currently being devoted to the synthesis of this type of novel porous aluminosilicate, which should overcome most of the adsorption/diffusion limitations of conventional Y zeolites and constitute a significant breakthrough in the field of inclusion chemistry.[3]

Recently we have reported that 2,4,6-triphenylpyrylium (TP$^+$), a well-documented electron transfer photosensitizer,[4-7] can be encapsulated as framework charge-compensating cation within the zeolite Y supercages.[8] The resulting composite (TPY) is able to promote the isomerization of *cis*-stilbene (CS) to *trans*-stilbene (TS) through a radical cation mechanism (Scheme 1).[9] This well-documented isomerization cannot occur through an energy transfer mechanism between 2,4,6-triphenylpyrylium and *cis*-stilbene, due to the energy values of the triplets involved (E_T = 53 and 60.3 kcal/mol, respectively), which would make this process energetically uphill.

Although a higher contribution of in-cage isomerization was shown to be characteristic of the intrazeolite process, the overall chemical yield of *trans*-stilbene using the pyrylium salt imprisoned within zeolite Y was far from optimum, owing to the diffusional restrictions imposed on the reagents by the faujasite.

Scheme 1. Contribution of the In-Cage (a) and Free Ion (b) Pathways to the TP$^+$-Photosensitized Isomerization of CS.



In the present communication, we report that the use as host of the novel aluminosilicate MCM-41[10] with 2-nm monodirectional channels hexagonally arranged opens new possibilities to carry out efficiently photoinduced electron transfer reactions. This is illustrated here by showing that the incorporation of 2,4,6-triphenylpyrylium cation in MCM-41 results in a remarkable increase of the chemical yield for the *cis*-stilbene isomerization compared with the analogous homogeneous irradiation or with the mere deposition of its tetrafluoroborate salt onto an amorphous siliceous material.

The required MCM-41 crystalline aluminosilicate was synthesized according to the reported procedure[11] by using amorphous silica (Aerosil 200, Degussa), a 25% aqueous solution of tetramethylammonium hydroxide, and an aqueous solution of hexadecyltrimethylammonium bromide as templates. The Si:Al ratio of the sample was 95 as determined by chemical analysis, while the pore diameter measured by Ar adsorption was 2 nm. 2,4,6-Triphenylpyrylium cation was synthesized by stirring a 2:1 mixture of chalcone and acetophenone[12] in isooctane at 383 K in the presence of MCM-41 for 11 days. The resulting yellow solid (TPM-41A) was submitted to exhaustive solid–liquid extraction using CH$_2$Cl$_2$. Formation of the pyrylium heterocycle was ascertained by FT-IR spectroscopy and UV–vis diffuse reflectance of the solid. The amount of organic cation formed in TPM-41A was 10.3 wt %, as estimated by thermogravimetric analysis. Although IR spectroscopy has shown that MCM-41 possesses a weak acidity,[13] our ship-in-a-bottle synthesis of 2,4,6–triphenylpyrylium establishes that the sites of this aluminosilicate are acid enough to catalyze the classical Claisen–Schmidt aldolic condensation. Alternatively, this cationic dye was directly incorporated by submitting an MCM-41 sample to ion exchange using 2,4,6-triphenylpyrylium tetrafluoroborate in CH$_2$Cl$_2$ (TPM-41B). The difference between the initial and the recovered amount of the tetrafluoroborate salt after ion exchange revealed that the content of this TPM-41B sample in pyrylium cation was 13.7 wt %. A schematic representation of the cationic sensitizer and *cis*-stilbene incorporated within the channels of this zeotype is presented in Figure 1.

In order to evaluate the degree of confinement within the mesopores of MCM-41 and its influence on the electron transfer *cis*-stilbene isomerization, a control sample (TPSA) was prepared by deposition of 2,4,6-triphenylpyrylium tetrafluoroborate onto an amorphous silica–alumina with 650 m^2 g^{-1} of surface area. The pyrylium content of the resulting TPSA sample was 21.4 wt %.

The results attained in the *cis*-stilbene isomerization upon long wavelength irradiation in the absence of oxygen using the pyrylium-containing photosensitizers are summarized in Table 1. Control experiments showed that no isomerization takes place in the presence of these heterogeneous sensitizers under the same conditions in the dark or under irradiation (λ > 350 nm) in the presence of NaY.

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[1] Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer, Parts A-D*; Elsevier: Amsterdam, 1988.

[2] Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321-339.

[3] Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111-115.

[4] Miranda, M. A.; García, H. *Chem. Rev.* **1994**, *94*, 1063-1089.

[5] Adam, W.; Denninge, V.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang, G. *J. Am. Chem. Soc.* **1992**, *114*, 5027-5035.

[6] Adam, W.; Walter, H.; Chen, G.-F.; Williams, F. *J. Am. Chem. Soc.* **1993**, *115*, 3007-3014.

[7] Adam, W.; Sendelbach, J. *J. Org. Chem.* **1993**, *58*, 5310-5315.

[8] Corma, A.; Fornés, V.; García, H.; Miranda, M. A.; Primo, J.; Sabater, M. J. *J. Am. Chem. Soc.* **1994**, *116*, 2276-2280.

[9] Gessner, F.; Scaiano, J. C. *J. Photochem. Photobiol., A* **1992**, *67*, 91-100.

[10] Behrens, P.; Stucky, G. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 696-699.

[11] Beck, J. S.; Vartulli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834-10843.

[12] Dimroth, K.; Reichardt, C.; Vogel, K. *Org. Synth.* **1969**, *49*, 121-124.

[13] Corma, A.; Fornés, V.; Navarro, M. T.; Pérez-Pariente, J. *J. Catal.* **1994**, *148*, 569-574.

0002-7863/94/1516-9767$04.50/0

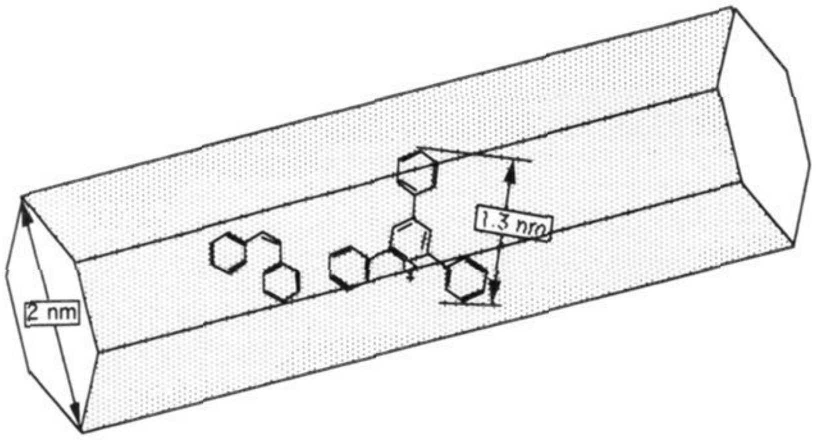

Figure 1. Schematic visualization of 2,4,6-triphenylpyrylium and *cis*-stilbene incorporated within the channels of MCM-41.

Table 1. Results of the *cis*-Stilbene (CS) Isomerization Using Different Photosensitizers Containing 2,4,6-Triphenylpyrylium Cation (TP^+)

sensitizer[a]	TS yield (%)[b]
$TP^+BF_4^-$ [c]	18
TPY[d]	7
TPM-41A	86
TPM-41B	68
TPSA	39

[a] Irradiations of CS (10^{-2} M) in CH_2Cl_2 were carried out simultaneously by stirring under Ar in the presence of the corresponding photosensitizer for 4 h, filtering ($\lambda > 350$ nm) the light from a 400-W mercury lamp. [b] The amount of TP^+ was ca. 2.5×10^{-5} M in all cases, corresponding to the following weights of each sensitizer: 8 mg of $TP^+BF_4^-$, 110 mg of TPY, 60 mg of TPM-41A, 45 mg of TPM-41B, and 28 mg of TPSA, respectively. [c] Under homogeneous conditions in CH_2Cl_2 solution. [d] Prepared as reported in ref 8.

From these data it appears that the efficiency of the MCM-41 host arises from the combination of the benefits derived from the restricted microenvironment of zeolites (retardation of back electron transfer) plus a better diffusion of reactants and products through the channels owing to their relative large dimensions. The latter effect is clearly demonstrated considering that the activity of the pyrylium cation within MCM-41 is 1 order of magnitude higher than within zeolite Y under the same experimental conditions.

On the other hand, differences in the efficiency of TPM-41A and TPM-41B may reflect a more uniform distribution of the sensitizer through the channels when pyrylium salt is synthesized "in situ" than when it is incorporated by ion exchange.

To further assess that most of the photosensitizer was indeed confined within the mesopores of the MCM-41, ruling out that pyrylium guest is located exclusively at the external surface, the irradiation of *cis*-stilbene/TPM-41B was performed in the presence of different amounts of azulene (Az) (Figure 2). This compound has been shown to be a suitable quencher for the isomerization of *cis*-stilbene at the stage of free radical cation (pathway b in Scheme 1). By contrast, it appears that "in-cage" isomerization (pathway a) is not affected by addition of this quencher.[8,14] As a matter of fact (Figure 3), the contribution of the latter pathway was higher for the TPM-41B-photosensitized reaction than for the analogous process under homogeneous conditions using the tetrafluoroborate salt in CH_2Cl_2 solution. As expected, the cage effect was proportionally even higher when TPY was used.

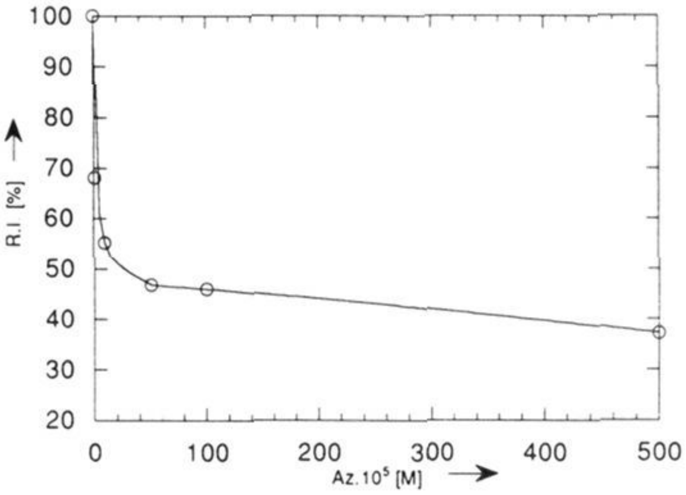

Figure 2. Plot of the percentage of residual CS-to-TS photosensitized isomerization (R.I.) vs the concentration of the azulene quencher (Az) using TPM-41B sensitizer in CH_2Cl_2. R.I. is defined as the chemical yield of TS in the presence of a particular concentration of Az divided by the TS chemical yield when Az is absent.

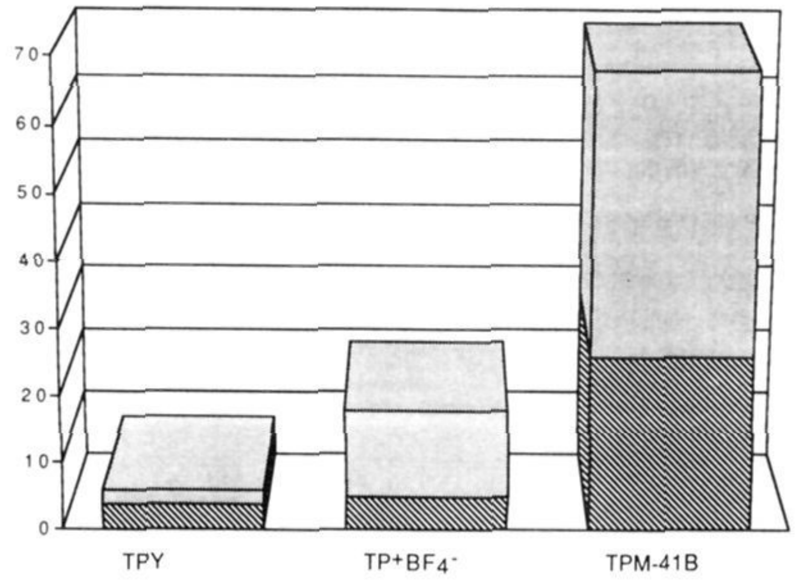

Figure 3. Chemical yields for the photosensitized CS isomerization showing the contributions of the "in-cage" and "free ion" routes. The values of the "in-cage" isomerization correspond to the measured TS chemical yields when Az concentration is higher than 10^{-3} M. The lower, darker part and the upper, lighter part of the columns correspond to pathways a and b of Scheme 1, respectively.

In summary, we have shown that extra large pore zeolitic aluminosilicates are very promising hosts to perform photoinduced electron transfer reactions. This seems to be the result of an adequate balance between moderate cage effect and facilitation of molecular traffic through the mesopores.

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Supplementary Material Available: X-Ray diffraction of MCM-41 after calcination at 823 K, aromatic region of the FT-IR spectrum of the TPM-41A sample after outgassing under vacuum for 1 h at room temperature (a), 100 °C (b), 200 °C (c), 300 °C (d), and 400 °C (e), successively, diffuse reflectance of the TPM-41A samples, and thermogravimetry (TG)–differential scanning calorimetry (DSC) of the TPM-41A sample (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Kuriyama, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1988**, 1193–1196.