

Photoinduced Electron Transfer within Zeolite Cavities: *cis*-Stilbene Isomerization Photosensitized by 2,4,6-Triphenylpyrylium Cation Imprisoned inside Zeolite Y

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Abstract: 2,4,6-Triphenylpyrylium cation (TP⁺), a well-established photoinduced electron-transfer sensitizer, has been encapsulated in the Y zeolite as a charge-compensating cation by ship-in-a-bottle acid-catalyzed reaction of chalcone with acetophenone in isooctane at 383 K. Formation of TP⁺ was ascertained by FT-IR spectroscopy and diffuse reflectance UV-vis spectrophotometry of the canary yellow-colored solid. Estimation of the TP⁺ content by the reaction stoichiometry, thermogravimetric analysis, and pyridine titration of the remaining Brønsted sites indicates that approximately one-third of the latter are compensated by TP⁺ cations. FT-IR monitoring of the OH stretching bands of both original acidic HY and the TPY samples reveals that TP⁺ cations are mainly exchanging Brønsted sites of the supercavities, while pyridine adsorption shows that the rest of the cavities are still accessible to this base. A molecular modeling visualization of the TP⁺ imprisoned in the Y supercavity has been carried out by docking, using the Biosym Insight II package. TPY shows moderate activity as an electron-transfer photosensitizer, being able to promote the isomerization of *cis*-stilbene to *trans*-stilbene via the corresponding radical cations. The reaction is not perturbed by the presence of oxygen, as evidenced by the absence of byproducts arising from oxidative cleavage. This contrasts with the extensive photooxygenation produced by 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) under homogeneous conditions. A higher contribution of the in-cage isomerization, associated with a retardation of back electron transfer in the radical ion pairs, appears to be the most noticeable characteristic of the intrazeolite process.

Introduction

The kinetics of photoinduced electron transfer (PET) in homogeneous solution involves the intermediacy of several donor-acceptor (DA) species, characterized by the intermolecular DA distance and the degree of charge separation. Thus, after completion of the electron-transfer step, the existence of contact ion pairs (CIP), solvent-separated ion pairs (SSIP), and free ions (FI) has been evidenced. Detailed mechanistic studies based mostly on quenching experiments have established that some chemical events occur exclusively at the CIP, SSIP, or FI stage.¹⁻³ Hence, it should be possible to modify the activity and selectivity of a PET process if the relative contributions of these intermediates could be somehow controlled.

The reaction efficiency in photoactivated systems depends largely on the minimization of back electron transfer (BET), a critical process which is decisively influenced by environmental variations.³ In the last years, zeolite cavities have been employed as microscopic reactors to control the photochemical behavior of organic molecules and to generate long-lived radical cations from their neutral precursors.⁴⁻⁶ In particular, the recent finding that the zeolite supercage can be used to strongly modulate the magnitude of the BET rate constant has constituted a significant breakthrough.⁷ Ion exchange of NaY with different organic cations (tropylium, methyl viologen, etc.) has led to doped zeolites

which, upon photochemical excitation, behave as electron acceptors toward suitable arene donors. The resulting ion pairs are strongly stabilized within the zeolite supercage, and their lifetimes are unusually high as compared with those previously measured in solution.⁷

In view of these precedents, it appeared interesting to prepare tailor-made zeolite-based electron-transfer photosensitizers in order to exploit the promising potential of these materials to achieve specific chemical transformations. A very attractive challenge was to place bulky organic cations in the internal zeolite supercavities by ship-in-a-bottle synthesis and to determine in an unambiguous way their location and accessibility. The extreme immobilization of the ET complexes could produce unforeseeable chemical consequences, and, on the other hand, the imprisonment of the organic sensitizer within the solid would be very convenient from the practical point of view, simplifying its separation from the reaction mixtures. In the present communication, we show how this idea can be materialized by using the Brønsted sites of HY zeolites to catalyze the ship-in-a-bottle synthesis of 2,4,6-triphenylpyrylium cation (TP⁺), a well-established electron acceptor in its excited state.⁸⁻¹³ Preliminary experiments show that this material (TPY) photosensitizes the isomerization of *cis*-stilbene (CS) to *trans*-stilbene (TS) via the corresponding radical cations, exhibiting some differential features with respect to the analogous process promoted by 2,4,6-triphenylpyrylium

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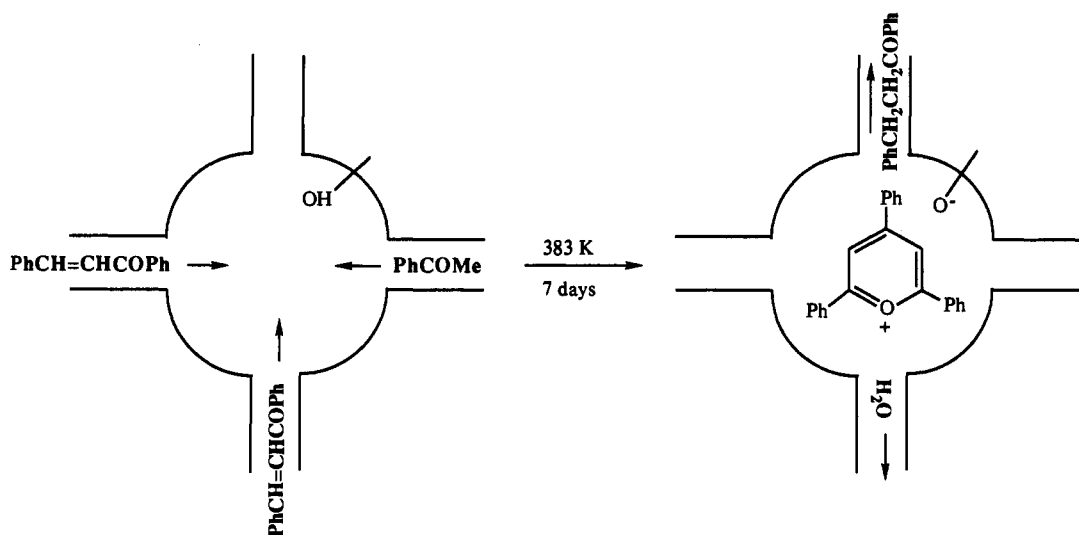


Figure 1. Synthesis of TPY from chalcone and acetophenone inside Y zeolite.

tetrafluoroborate (TPT) in homogeneous solution.^{14,15} The results obtained suggest an enhanced contribution of the in-cage isomerization, associated with a retardation of back electron transfer in the radical ion pairs for the intrazeolite PET process.

Results and Discussion

By means of a molecular modeling program,¹⁶ it was found that TP^+ cannot enter through the 0.8-nm cavity windows, and accordingly initial attempts to introduce TP^+ by ion exchange into the zeolite were unsuccessful. Therefore, we tried to synthesize TP^+ directly inside the zeolite cavities, by emulating the HBF_4 -catalyzed reaction of chalcone with acetophenone (in a molar ratio 2:1).¹⁷ In this case an acid Y zeolite was used instead of HBF_4 , in the hope that its Brønsted acid sites could act at the same time as catalysts and as counterions to be replaced by TP^+ (Figure 1).

The FT-IR spectrum of the yellow TPY zeolite sample after dehydration matched with that of a pure sample of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT), showing that TP^+ had been formed free from any residual precursor (Figure 2). A diffuse reflectance UV-vis spectrum of the TPY sample (Figure 3) was also identical to the very characteristic spectrum of TPT in CH_2Cl_2 solution. Moreover, the FT-IR spectra of TPY (not shown) after thermal treatment under vacuum remained substantially unchanged below 573 K, indicating the high stability of TP^+ hosted within the structure of the Y zeolite. This finding was in good agreement with the thermogravimetric analysis of the TPY sample, which showed a weight loss of 5.5% between 573 and 873 K (Figure 4). This result was corroborated by the reactants' mass balance and is compatible with the pyridine adsorption results which are discussed below.

Once formation and quantification of TP^+ were ensured, it was of interest to determine the location of TP^+ and its accessibility on the solid. Since the mobility of this bulky cation throughout the zeolite framework must be severely restricted, its location was especially relevant in determining the sites where PET can occur. It was anticipated that TP^+ placed on the external surface of the solid, while easily accessible to donor molecules from the solution, should behave in a different way than internal TP^+ ,

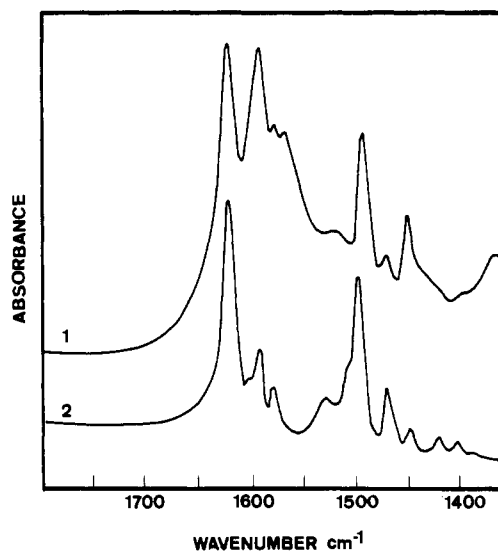


Figure 2. FT-IR spectra in the region between 1800 and 1350 cm^{-1} of TPT (trace 2) and the TPY zeolite after thermal dehydration at 10^{-3} Pa for 2 h at 573 K (trace 1).

owing to the characteristic properties of the intrazeolite microenvironment (cage effect, electrostatic fields, etc.).^{4,18,19}

In order to address these questions, a more detailed FT-IR spectroscopic analysis was performed on the starting HY-100 and the TPY samples. In fact, TP^+ cations of TPY must be replacing a portion of the protons located at the zeolite supercages, and hence a decrease in the intensity of the IR-absorption bands associated to acidic OH groups (3630 cm^{-1})²⁰ with respect to the original HY-100 zeolite should be observed. Moreover, adsorption of pyridine on HY-100 and TPY should allow an estimation of the number of accessible Brønsted acid sites on both samples.²¹

As a matter of fact, a comparison of the spectra in the OH region (not shown) indicated that mainly internal protons of the original HY-100 had been substituted by TP^+ in the TPY zeolite and that the remaining acid sites were still accessible to pyridine.

To improve resolution, a similar dealuminated Y sample (HY-F) was used, after treatment with $(NH_4)_2SiF_6$ at 363 K in order

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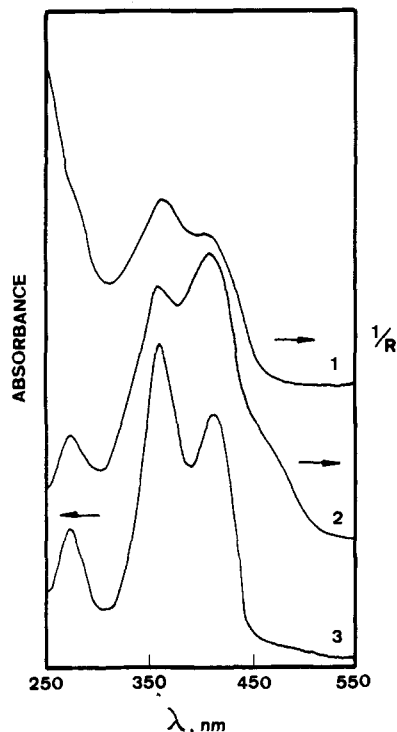


Figure 3. Diffuse reflectance UV-vis spectra of the TPY sample (trace 1) and BaSO₄/TPT (trace 2) together with the UV-vis spectrum of a 10⁻⁴ M solution of TPT in CH₂Cl₂ (trace 3).

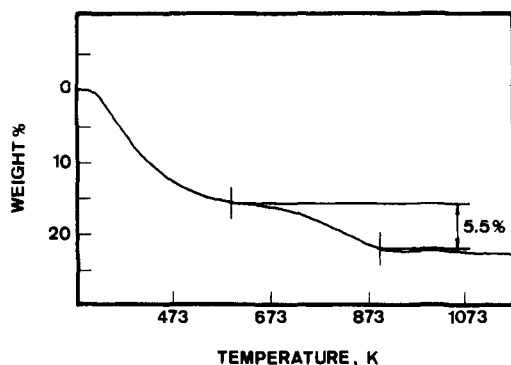


Figure 4. Thermogravimetric analysis of the TPY sample.

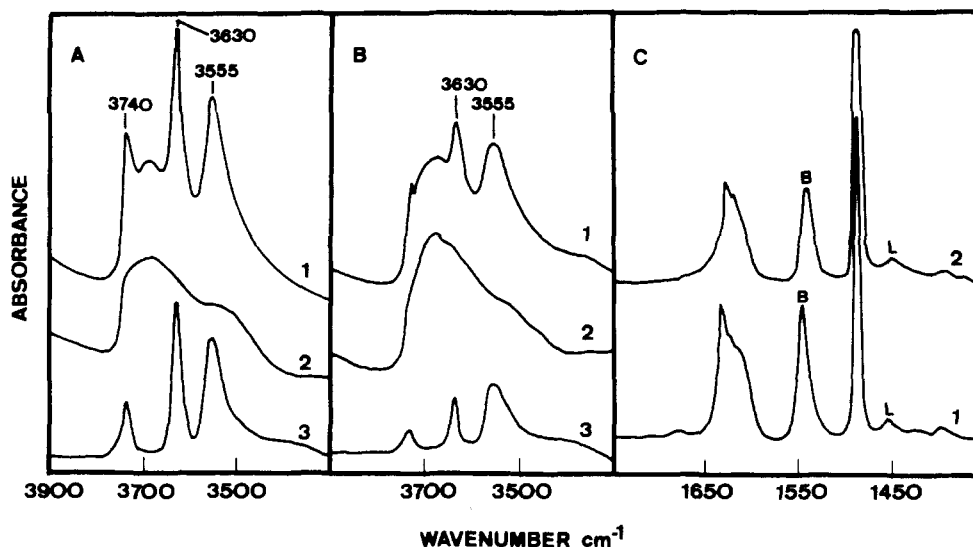


Figure 5. FT-IR spectra between 3900 and 3300 cm⁻¹ of the samples HY-F (A) and TPY (B). (Trace 1) After treatment at 573 K and 10⁻³ Pa for 2 h; (trace 2) after pyridine adsorption at room temperature followed by desorption at 423 K and 10⁻³ Pa for 1 h; and (trace 3) difference spectra, trace 1-2. (C) FT-IR spectra (1700-1400-cm⁻¹ region) of pyridine adsorbed on HY-F (trace 1) and TPY-F (trace 2) obtained by subtracting the spectra recorded before pyridine adsorption.

to remove most of the extraframework aluminum (EFAL) from the zeolite.^{22,23} Preparation of TPY-F was accomplished as indicated above for TPY. Formation of TP⁺ was confirmed by FT-IR and diffuse reflectance UV-vis spectroscopy and indicated that the presence of Lewis acid sites on the zeolite, not present in this sample, are not strictly necessary to catalyze this condensation. As expected, the FT-IR spectra of the HY-F and TPY-F samples showed well-resolved bands for each type of OH (Figure 5A and B). Their comparison confirmed an important diminution of the intensity of the bands corresponding to the acid OH, mainly those located at the supercages (3630 cm⁻¹). Therefore, it must be concluded that most of the zeolite-bound TP⁺ is replacing acid Brønsted sites of the internal supercavities.

Moreover, pyridine adsorption monitored by FT-IR spectroscopy revealed that all the types of Brønsted sites remaining on the TPY-F were still accessible and that TP⁺ was not blocking the micropores of the zeolite crystal (Figure 5B). In addition, according to the intensities of the 1550-cm⁻¹ pyridinium band (Figure 5C), it was established that the TPY-F sample adsorbs approximately one-third less pyridine than the corresponding starting HY-F zeolite, showing again that roughly one-third of the supercages are filled with TP⁺.

Figure 6 represents the visualization of the TP⁺ cation imprisoned within the faujasite supercage by using a molecular modeling program. The most important point is that this bulky cation can be easily accommodated inside the 1.3-nm spherical cavity, and one of the four tetrahedrally arranged 0.8-nm windows connecting the cavities lies just over the core of the pyrylium ring, allowing contact between TP⁺ and potential donor molecules during the PET process.

The one-way transformation of *cis*-stilbene ($E_{D^+/D} = 1.59$ V vs SCE) to its *trans* isomer *via* radical cation (Scheme 1) was chosen as a model reaction to check the suitability of TPY as a heterogeneous electron-transfer photosensitizer. This is a well-documented process,^{6,14} which presents several advantages, including (a) the inability of *trans*-stilbene radical cation to undergo the reverse reaction, (b) the endothermicity of the energy transfer between TPT ($E_T = 53$ kcal/mol) and *cis*-stilbene ($E_T = 60.3$ kcal/mol), and (c) the easy determination of the relative ratios of both isomers by means of GC analysis.

Irradiation ($\lambda > 400$ nm) of a 10⁻² M solution of CS in CH₂Cl₂ for 4 h under argon in the presence of TPY and TPT resulted in partial isomerization to TS (19% and 30%, respectively). In solution, electron transfer occurs from CS to the T₁ state of TPT,

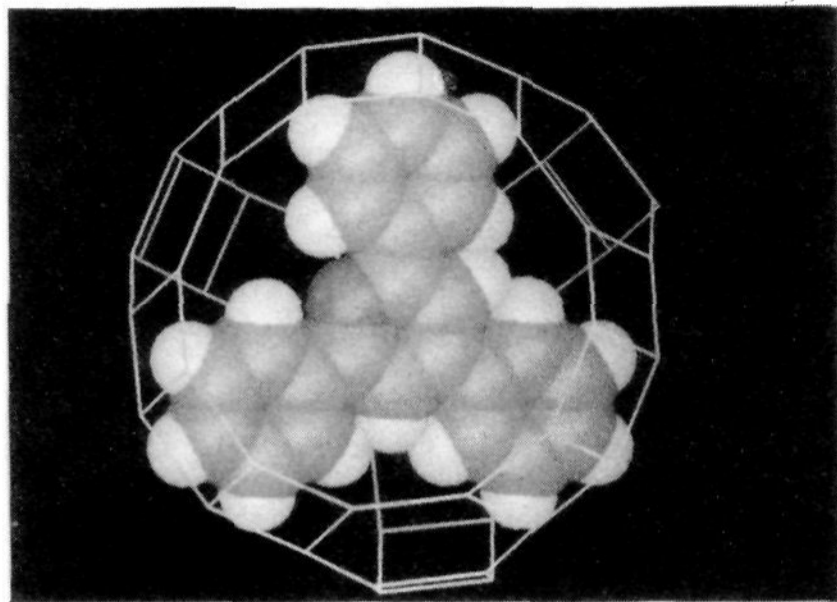
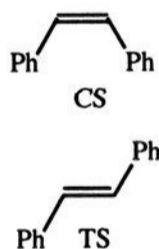
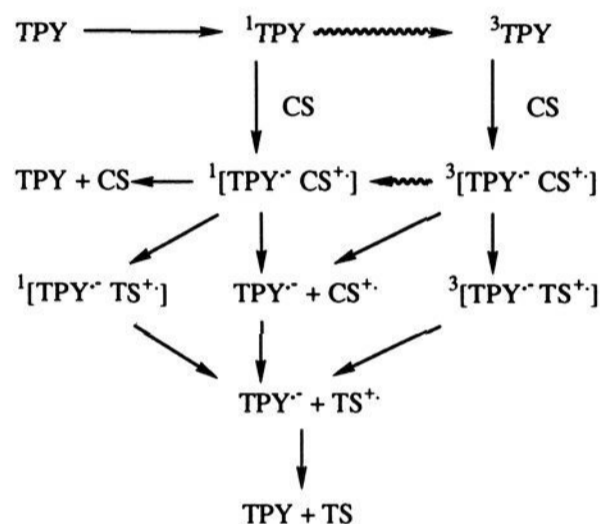


Figure 6. Molecular graphics representation of the TP⁺ cation included in the α -cage of the Y zeolite. The phenyl groups are directed to the entrance windows of the cages, partially penetrating the channels. The TP⁺ cation must be prepared by ship-in-a-bottle synthesis because of its restricted diffusion between the zeolite cavities.

Scheme 1



after intersystem crossing from the S_1 . A competing process is quenching of the TPT singlet by *cis*-stilbene, which does not result in isomerization due to an efficient, energy wasting, back electron transfer within the resulting singlet radical ion pair.^{14,24} Quenching is a bimolecular process and must increase with the CS concentration, while ISC unimolecular. Inside the zeolite, the concentration of CS is higher than in the liquid phase (concentration effect),²⁵ and on the other hand, diffusion becomes slower;²⁵ this explains the lower rates observed for *cis*-*trans* isomerization under heterogeneous PET conditions. As expected,¹⁴ the isomerization efficiency decreased with CS concentration (Figure 7).

A further point of concern was to determine the magnitude of the cage effect in the heterogeneous TPY reaction. This was achieved using azulene ($E_{Q^+/Q} = 0.95$ V vs SCE) to quench the out-of-cage fraction of TPT-photosensitized CS isomerization (Figure 8). When increasing amounts of azulene were added to

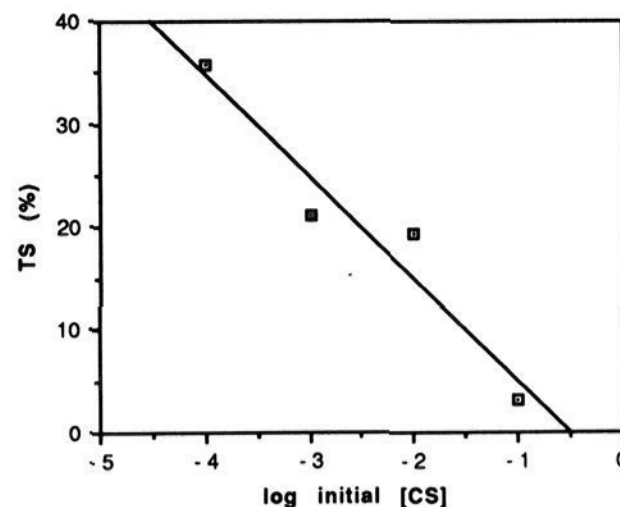


Figure 7. TPY-photosensitized isomerization of CS to TS at different CS concentrations.

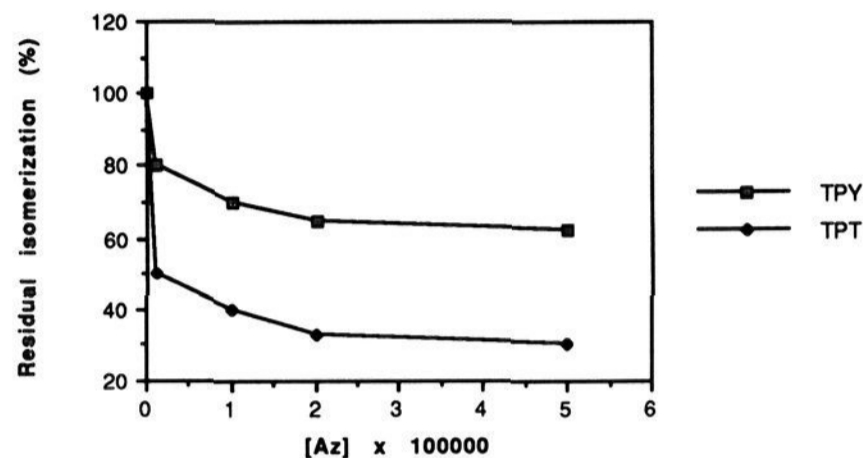


Figure 8. Partial inhibition of the TPT or TPY photosensitized isomerization of CS by azulene (Az). Residual isomerization reflects the contribution of the in-cage process.

the CS/TPY suspensions, the degree of isomerization progressively decreased to ca. 60% of the initial value. This residual percentage reflects the contribution of the in-cage process and is significantly higher than the value (30%) obtained in the homogeneous TPT reaction. Such an effect was not unexpected, since the radical cations CS^{•+} formed as a consequence of the electron transfer to excited TP⁺ become the charge compensating cations of the zeolite, which means that they should be considerably immobilized, and their diffusion must be slowed. Taken as a whole, the above facts strongly suggest that charge separation occurs to a considerable extent inside the zeolite supercages, facilitated by an enhanced lifetime of the initially formed radical pairs and by retardation of back electron transfer.

It has been reported that TPT photosensitizes oxygenation of stilbenes *via* trapping of their free radical ions by molecular oxygen.²⁶ According to this picture, the TPY-promoted photoisomerization of CS to TS should be less perturbed by the presence of oxygen than the analogous TPT reaction, owing to the different contribution of the in-cage electron transfer. In fact, when the heterogeneous system containing TPY and CS was irradiated in the presence of oxygen, TS was obtained in 21% yield, free from any byproducts of oxidative cleavage; by contrast, the use of TPT under homogeneous conditions led to a small amount of TS (2%) and produced extensive photooxygenation (mainly to benzaldehyde). This constitutes an additional support in favor of our mechanistic proposals and illustrates the dramatic changes in product selectivity which can be associated with intrazeolite PET processes.

Conclusion

The 2,4,6-triphenylpyrylium cation has been encapsulated within Y zeolite by ship-in-a-bottle synthesis from chalcone and acetophenone. FT-IR monitoring of the OH stretching bands of both original acidic HY and the TPY samples reveals that TP⁺

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cations are mainly exchanging Brønsted sites located at the supercavities, and pyridine adsorption shows that the rest of the protons are still accessible to this base. This material (TPY) shows moderate activity as an electron-transfer photosensitizer, as evidenced by the isomerization of CS to TS *via* the corresponding radical cations. A higher contribution of the in-cage isomerization, associated with a retardation of back electron transfer in the radical ion pairs, is the most noticeable characteristic of the intrazeolite process.

Experimental Section

Preparation of Zeolites. The acid HY-100 sample was prepared¹⁸ starting from commercial NaY (SK-40, Union Carbide) by three consecutive Na⁺-to-NH₄⁺ exchanges, followed by steam calcination (773 K, 2 h). Chemical analysis showed that the Na₂O content was less than 0.15 wt %, the average crystal size was 0.8 μm, as measured by SEM, and X-ray diffraction showed that the crystallinity was 85%, with a unit cell size of 2.441 nm according to the ASTM D-3942-8 protocol. Treatment of a mixture of chalcone (410 mg) and acetophenone (120 mg) in isooctane (50 mL) at 383 K in the presence of HY-100 (1.00 g) during a week, followed by exhaustive solid-liquid extraction (CH₂Cl₂) of the solid using micro-Soxhlet equipment, allowed the separation of a liquid phase containing dihydrochalcone and 1,3,5-triphenyl-1,5-pentanedione from a solid phase formed by the functionalized Y zeolite (TPY), which became canary yellow-colored.

Characterization of the TPY Sample. IR spectra of the samples were carried out in a greaseless IR quartz cell fitted with CaF₂ windows, using a Nicolet 710 FT-IR spectrophotometer. For pyridine adsorption measurements, the samples were previously treated under vacuum at 573 K for 15 h. Pyridine (6.6 × 10⁻² Pa) was then admitted in the cell at room temperature and degassed under vacuum at 423 K for 1 h. All spectra were obtained at room temperature.

Diffuse reflectance UV-vis spectra were recorded with a Shimadzu UV-2101/3101 PC scanning spectrophotometer. Thermogravimetric analyses were performed with a Netzsch-STA 409 EP thermobalance.

Irradiation Procedure. TPY (10⁻⁵ equiv) was added to CH₂Cl₂ (5 mL) containing 10⁻² M *cis*-stilbene, and the resulting suspensions were magnetically stirred while being irradiated for 4 h with the K₂CrO₄-filtered light (λ > 400 nm) of a medium-pressure mercury lamp to ensure selective absorption by the yellow zeolite-bound sensitizer. Parallel experiments were carried out under homogeneous conditions using the same amount of soluble TPT. Analysis of reaction mixtures was performed by GC (Hewlett-Packard 5890 provided with a 25-m capillary column of crosslinked 5% phenylmethylsilicone), GC-MS (Hewlett-Packard 5988 A spectrometer), and GC-FT-IR (Hewlett-Packard 5890 GC coupled with a 5965 A FTIR detector).

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