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# Zeolite-based Heterogeneous Photosensitizers Containing Triphenylpyrylium and Dibenzotropylium Cations. Modifications of the Product Selectivity in the Cyclodimerization of 1,3-Cyclohexadiene

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***Abstract.*** Triphenylpyrylium ($TP^+$), and dibenzo[a,d]tropylium ($DT^+$) cations have been incorporated inside zeolites, and their potential as heterogeneous photosensitizers has been examined using the PET-cyclodimerization of 1,3-cyclohexadiene (CHD) as test reaction. The behaviour of zeolites containing $TP^+$ as heterogeneous photosensitizers was compared with the results obtained in homogeneous solution using the soluble $TP^+$ tetrafluoroborate salt (TPT). With the cation encapsulated within Y zeolite the reaction proceeded slower, presumably due to light scattering and mobility restrictions associated with the diffusion difficulties in the solid. Accordingly, inside the extra large pore MCM-41 the reaction efficiency was enhanced by a factor of 9, although it remained lower than in the homogeneous system. As in solution, the *endo* [4+2] adduct was the major product. When a La-exchanged Y zeolite containing $TP^+$ was used, the degree of conversion was even lower. This suggests that CHD cyclodimerization must occur *via* electron transfer to singlet $TP^+$. In the case of $DT^+$ within ZSM-5, the selectivity was reversed with respect to $TP^+$: the major product was the *anti* [2+2] dimer. This was attributed to generation of $^3$CHD as the result of back electron transfer at the $^1[CHD^{+\cdot}/DT^{\cdot}]$ stage.

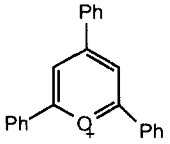
## INTRODUCTION

Zeolites have been found to be very convenient hosts to control and modify the photochemistry of adsorbed organic compounds.[1-3] Besides a passive role defining the shape, size and flexibility of the reaction cavity[4] the versatility of zeolites can be increased by their possible active role, providing the sites required in photochemical transformations.[5-8]

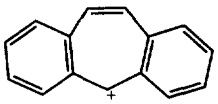
Until now, the applications of zeolites in photochemistry have been focused on the direct photolysis of adsorbed guests, while the possibility of performing photosensitized chemical reactions in such organized media remains essentially unexplored. Since this requires some kind of encounter between the sensitizer and the reacting compound, immobilization of the former within the micropores appears necessary to define a stationary and constant reaction cavity. In addition , the photochemical reaction can be carried out by stirring a slurry of the sensitizer-containing zeolite in an inert liquid phase. This can be advantageous from the experimental point of view, since it avoids the leaching out of the sensitizer and makes easier the work-up and isolation of the photoproducts.

The presence of charge-balancing cations within the internal voids of the micropores makes zeolites especially appropriate to incorporate cationic sensitizers. Very recently, we have shown[9,10] that 2,4,6-triphenylpyrylium ($TP^+$) cation, a well-documented electron transfer (ET) photosensitizer,[11] can be synthesized within the supercages of faujasite or incorporated inside extra large pore materials such as MCM-41. These solids are suitable hosts to perform heterogeneous photoinduced electron transfer (PET) reactions, increasing the contribution of in-cage pathways to the overall photochemical reaction. In this context, transient studies have observed an extraordinary increase of the radical ion pair lifetime as consequence of its stabilization within the faujasite supercages and the retardation of back electron transfer (BET).[12] However, experimental examples where photochemical generation of radical ion pairs within the zeolite microenvironment leads to a modification of the product pattern are still scarce.

In the present work we have prepared and characterized dibenzo[a,d]tropylium ($DT^+$) cations on zeolites and examined their behaviour, together with that of the above mentioned $TP^+$-containing zeolites, as potential heterogeneous photosensitizers. It has been reported that singlet and triplet excited states of $DT^+$ can be quenched by suitable electron donors.[13] However, in most cases preparative experiments using $DT^+$ as PET-sensitizer have failed to isolate any well-defined products,[13] which has been attributed to a fast BET resulting in deactivation of the photogenerated radical ion pairs. Therefore, it appeared interesting to disclose whether the expected ET products can be formed in the zeolite microenvironment.



$TP^+$



$DT^+$

In order to determine the photosensitizing ability of $TP^+$ and $DT^+$ cations within zeolite media, the PET-cyclodimerization of 1,3-cyclohexadiene (CHD) was chosen as test reaction. It has been firmly established[14-17] that the preference for [2+2] or [4+2] dimerization pattern depends on the type of photosensitization (energy *versus* electron transfer, respectively). Furthermore, the different space demands of the bulky cyclodimers, in conjunction with the geometrical constraints impossed by the crystalline lattice, should have some influence on the dimer distribution when the reaction takes place within the internal voids of the solids. Additional advantages of this model are the relative inertness of CHD in acidic media and the availability of known data on the thermal and direct UV-photochemical reactivity of CHD within related NaX faujasite.[18]

## RESULTS AND DISCUSSION

### *Preparation and characterization of the photosensitizers*

The preparation and characterization of $TP^+$ within zeolites (Y and MCM-41) was done as previously described.[9,10] It is known that $DT^+$ cations can be conveniently generated in homogeneous liquid solution by treatment of dibenzosuberenol (DTOH) with acids such as sulfuric or trifluoroacetic.[19] Emulation of this reaction employing acid zeolites resulted a successful strategy to adsorb $DT^+$ within zeolites. The $H^+$-forms of Y and ZSM-5 were used as hosts. After adsorption, the zeolites were submitted to exhaustive solid-liquid extraction to avoid the presence of weakly adsorbed neutral organic material. The resulting red coloured solids were fully characterized by UV/Vis diffuse reflectance (DR), IR spectroscopy and thermogravimetric analysis-differential scanning calorimetry (TG-DSC). Thus, the presence of $DT^+$ was ascertained by comparison of the obtained DR spectra with the characteristic UV/Vis absorption spectra of this cation in solution (maxima at ca. 540, 515, 400 and 385 nm). Furthermore, the IR spectra recorded at room temperature, after outgassing at 473 K for 1 h, showed characteristic absorption bands at ca. 1600 and 1530 $cm^{-1}$ assignable to $DT^+$. These bands were identical to those obtained after addition of $H_2SO_4$ to a KBr disk of the corresponding alcohol and clearly different from those of untreated DTOH. A reasonable estimation of the $DT^+$ content in these samples (ca. 2% weight) could be obtained from the TG-DSC data. A comparison of the 3600-3400 $cm^{-1}$ IR spectra of the original $H^+$ zeolites with those of the samples containing $DT^+$ under exactly the same experimental conditions revealed an appreciable decrease of the acidic OH bands, thus indicating that some protons had been substituted by the organic cations. The lower thermal stability of $DT^+$ adsorbed onto acid zeolites is evidenced by the fact that the IR spectra of zeolites containing this cation, recorded at room temperature after treatment at 673 K, showed an almost complete disappearance of the $DT^+$ characteristic bands, together with the presence of typical absorptions at 1570 $cm^{-1}$ due to coke.[9]

Besides the thermal stability, another point of concern was the lifetime of $DT^+$ incorporated within zeolites. Zeolites are highly hydrophilic solids whose water content can be higher than 20 wt%. Therefore, a progressive hydration of the cations to give the corresponding DTOH alcohols was expected to occur inside zeolites. As a matter of fact, the presence of water within the solids was confirmed by FT-IR of the samples prior to thermal treatment, as well as by the initial TG-DSC traces (temperatures $\leq$473 K). Depending on the type of zeolite, between 8 and 15 % of the weight corresponds approximately to physisorbed water.

As anticipated, when Y zeolite was used as host, the characteristic colour of the solids progressively faded and eventually disappeared after several days (typically about 15 days). However, in the case of the analogous ZSM-5 samples no appreciable changes in the DR or FT-IR could be observed over a period of several months. These facts can be easily rationalized by assuming that the space requirements for the $H_2O$ attack over the cations are not met within the internal voids of this zeolite, so that the cations are effectively protected within the channels from external nucleophilic agents. By contrast, the much larger dimensions of the Y supercages allow approach of $H_2O$ to the electron-deficient centers. Nonetheless, the role of the strong internal electrostatic fields of zeolites stabilizing charged organic species has to be remarked again, since even in the case of the Y zeolite the reaction of $DT^+$ with water does not take place instantaneously.

### *Photosensitized CHD dimerizations*

Photolysis of CHD (50 mg) in $CH_2Cl_2$ (5 ml) was carried out for 12 h at room temperature, in the presence of the corresponding zeolite-cage cation (250 mg), with the filtered light ($\lambda \geq 400$ nm) of medium pressure mercury lamps (Table 1). The use of a filtering solution ($K_2CrO_4$) combined with Pyrex glass ensured that neither direct CHD irradiation nor sensitization by adventitious DTOH was taking place. Control experiments showed that no reaction occurred in the dark in the presence of zeolite hosts (with or without adsorbed organic cations). In order to minimize secondary reactions and avoid possible effects arising from deactivation of the zeolitic photosensitizers by blockage of the micropores, product distributions were compared at CHD conversions lower than 20%.

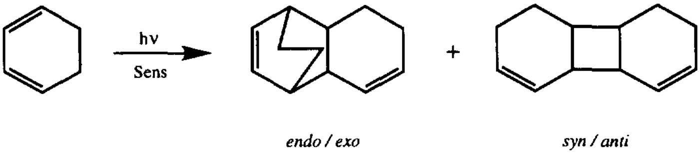


Table 1. PET- Cyclodimerization of Cyclohexadiene

| Entry | Sensitizer | Conversion % | Product distribution (%)[a]<br>[4+2]endo | [4+2]exo +[2+2]anti | [2+2]syn |
|---|---|---|---|---|---|
| 1 | TPT ( 8 mg ) | >98 | 88 | 12 | b |
| 2 | TPT (16 mg ) | >98 | 86 | 14 | b |
| 3 | TPT (24 mg) | >98 | 88 | 12 | b |
| 4 | TP-Y | 3 | 60 | 34 | 6 |
| 5 | TP-LaY | 1 | 44 | 48 | 8 |
| 6 | TP-MCM-41 | 28 | 68 | 28 | 4 |
| 7 | DT-ZSM-5 | 20 | 32 | 58 | 10 |

a: determined by GC. b: traces

In a first series of experiments, the behaviour of zeolites containing $TP^+$ as heterogeneous photosensitizers was compared with the results obtained in homogeneous solutions. Three different concentrations of the soluble $TP^+$ tetrafluoroborate salt (TPT) were used, in order to ascertain whether possible variations in the $TP^+$ content of the solids could produce significant alteration of the product pattern. This was found not to be the case (Table 1,entries 1-3). Within the employed TPT concentration range, CHD conversion remained consistently over 90% and the [4+2] dimers were the almost exclusive products, with a nearly constant *endo/exo* ratio of *ca.* 7. Predominance of the *endo* dimer is indicative of an electron transfer mechanism and has been previously observed upon chemical, photochemical or electrochemical generation of the radical cation $CHD^{+\cdot}$.[11] By contrast, cyclodimerization of CHD by means of triplet energy transfer leads to reaction mixtures where the *anti* [2+2] dimer is the major photoproduct. With the same cationic sensitizer ($TP^+$) encapsulated within Y zeolite different results were obtained (Table 1, entry 4). The reaction proceeded slower, presumably due to light scattering and mobility restrictions associated with the diffusion difficulties in the solid. Besides, detectable amounts of the [2+2] dimers were present in the photomixture, although the *endo* [4+2] adduct was still the major product. Its predominance over the *exo* isomer was less marked than in homogeneous phase, probably as a consequence of the enhanced cage effect, which should lead to a higher contribution of electron transfer within contact ion pairs (CIP) and disfavour formation of solvent separated ion pairs (SSIP) or free ions (FI).

Although most PET-sensitizers operate as electron acceptors after promotion to their excited singlet states, in the case of $TP^+$ both the excited singlet and triplet can participate in electron transfer.[11] This property is the result of an adequate conjunction of moderate intersystem crossing quantum yield with suitable reduction potential and excitation energies. Additionally, the triplet sensitizer might in principle be involved in energy transfer processes. This possibility cannot be safely ruled out for the $TP^+$/CHD pair in view of the slightly exothermic nature of the process. [20] In order to establish the multiplicity of the $TP^+$ excited state intervening in the PET-cyclodimerization of CHD, the organic cation was synthesized inside a La-exchanged Y zeolite. It is known that the external heavy atom effect in faujasite supercavities is highly efficient.[3] Hence, a decrease in the population of the $TP^+$ singlet state by the La-heavy atom was expected to produce some effect on the reaction efficiency. Actually, when this material was used as heterogeneous photosensitizer (Table 1, entry 5) the degree of conversion was somewhat lower than that achieved with the non-exchanged Y zeolite containing $TP^+$ (Table 1, entry 4). This suggests that most of the CHD cyclodimerization must occur *via* electron transfer to singlet $TP^+$, since in the case of triplet sensitization (either by electron or energy transfer) an enhanced conversion would have been observed under the same conditions.

In heterogeneous photoreactions using microporous systems, impeded diffusion of the reagents and accessibility of the sites are key limiting factors from the preparative viewpoint. In this connection, the diffusional restrictions associated with the relatively small size of the micropores (*ca.* 1.3 nm) must be related to the lower efficiency observed for CHD cyclodimerization with $TP^+$ within Y zeolites, as compared with the results obtained in solution. Therefore, it appeared interesting to perform an analogous experiment with the cationic sensitizer incorporated inside the extra large pore material MCM-41, whose 2-nm monodirectional channels hexagonally arranged might open new possibilities to overcome the above mentioned restrictions to molecular traffic in conventional zeolites. As anticipated, the reaction efficiency was enhanced by a factor of 9, although it remained lower than in the homogeneous system (Table 1, entries 1-3).

Finally, ZSM-5 zeolites containing $DT^+$ were also used as heterogeneous photosensitizers for CHD cyclodimerization (Table 1, entry 7). In this case, the *anti* [2+2] dimer was the major product, which suggested the involvement of a triplet pathway. Since energy transfer from $^3DT^+$ to CHD is clearly disfavoured from the thermodynamic point of view,[21] photosensitization must occur *via* electron transfer from CHD to excited $DT^+$.[13] The observed product selectivity would then be explained by the contribution of back electron transfer at the $^1[CHD^{+\cdot}/DT^\cdot]$ stage, which would give triplet CHD. Related precedents on BET of singlet radical ion pairs leading to triplets or biradicals can be found in the literature.[20]

In summary, the cations $TP^+$ and $DT^+$ within zeolites behave as ET-photosensitizers. From the preparative point of view, a major disadvantage is that the reactions proceed slower than in solution, due to light scattering and mobility restrictions associated with the diffusion difficulties in the solid. This can be less dramatic for intra- than for intermolecular processes (i.e., isomerization[9,10] *vs.* cycloaddition). Moreover, a possible strategy to overcome these limitations appears to be the use of material with extralarge pore dimensions such as MCM-41. On the other hand zeolite-based photosensitizers can be of great interest for mechanistic studies.[12]

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## EXPERIMENTAL

### *Adsorption pocedure*

DT-Y and DT-ZSM-5: A suspension of dibenzosuberenol (57 mg) in isooctane (25 ml) was poured onto the corresponding zeolite ( Y or ZSM-5) (1.00 g), previously activated at 100 °C during 4 h under vacuum. The resulting suspension was magnetically stirred at reflux temperature for 2 h. After this time, the solid was filtered, washed with fresh isooctane and then submitted to continuous solid-liquid extraction, using a micro-Soxhlet equipment and isooctane as solvent. The combined solutions were analyzed by GC-MS. The dry solid was characterized by UV-Vis diffuse reflectance, IR spectroscopy and thermogravimetric analysis-differential scanning calorimetry. Details of this methodology can be found elsewhere.[9]

TP-Y, TP-LaY and TP-MCM-41 were prepared following reported procedures.[9]

*Irradiation procedure*

Cyclohexadiene (50 mg ) in $CH_2Cl_2$ (5 ml) was stirred under Ar in with the corresponding zeolite -bound photosensitizer (250 mg ) and irradiated for 12 h with the light from a 250-W medium pressure mercury lamp, using a $K_2CrO_4$ solution ($\lambda > 400$ nm). After irradiation, the samples were analyzed by GC.The peaks corresponding to the *endo* [ 4+2 ] and the *syn* [ 2+2 ] dimers were well resolved; however the *exo* [ 4+2 ] and the *anti* [ 2+2 ] dimers gave rise to a single chromatographic peak. Their relative ratio was established in some cases by 1H-NMR spectroscopy, through the characteristic signals assignable to olefinic and allylic protons.

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