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Intrazeolite Photochemistry. 21. 2,4,6-Triphenylpyrylium Encapsulated inside Zeolite Y Supercages as Heterogeneous Photocatalyst for the Generation of Hydroxyl Radical

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The hydroxyl radical is among the most reactive species in chemistry, and it is a key intermediate in cellular oxidative stress[1,2] and in advanced oxidation techniques for the remediation of polluted wastewaters.[3] The wide use of TiO_2 as photocatalyst and Fenton-like processes as general methodologies to degrade organic material is based on the intermediacy of $OH^\bullet$ radicals.[4,5] The development of new methods of generation of $OH^\bullet$ radicals and their detection using time-resolved techniques is of interest.[6,7]

Herein, we report a heterogeneous photocatalytic system consisting of 2,4,6-triphenylpyrylium ion (TP^+) encapsulated inside the supercages of Y zeolite (TPY) that generates $OH^\bullet$ radicals in the presence of water.

In principle, a general, viable strategy to form $OH^\bullet$ radicals would be the generation of $H_2O^{+\bullet}$ by the photoinduced electron transfer (PET) from water to a suitable excited electron acceptor (ET step in Scheme 1). However, despite the relatively low oxidation potential of water (1.28 V vs SCE, pH 5.7), this methodology has not been exploited in full owing to a combination of negative factors including degradation of the photosensitizer and solubility problems.[8]

The organic TP^+ tetrafluoroborate salt ($[TP^+BF_4^+]$, TPT) is only sparingly soluble in water, where it undergoes nucleophilic addition of water to form 1,3,5-triphenylpent-2-en-1,5-dione (PDO). Even an aqueous suspension of TPT becomes totally hydrolyzed in a few hours. In acetonitrile/water mixtures (50/50), TPT is persistent enough to allow laser flash photolysis (LFP) studies.[9] Under these conditions, the only transient species observed is TP^+ triplet excited state and no evidence for the formation of $TP^\bullet$ was obtained (Figure 1A). Thus, under these conditions, no PET between TP^+ and H_2O takes places, although this process is predicted to be exergonic by the Rehm−Weller equation[10,11] and the wide use of TP^+ as electron-transfer photosensitizer.[12,13]

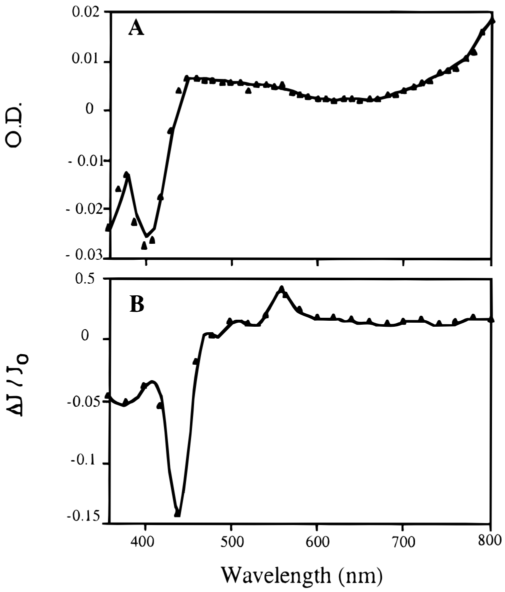
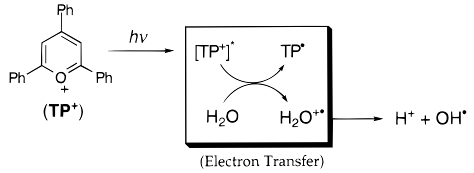


Figure 1. Transient spectra of TPT in CH_3CN/H_2O 90/10 (A, triplet excited state) and a TPY/H_2O slurry (B, $TP^\bullet$) after 355 nm laser excitation recorded at 1 and 10 μs, respectively.

Scheme 1



Pyrylium cleavage to PDO is totally supressed upon TP^+ incorporation inside the supercages of Y zeolite.[14] Thus, periodic controls by diffuse reflectance spectroscopy of TPY stirred in water did not show any noticeable change in the intensity of the characteristic TP^+ absorption bands (λ 370 and 420 nm) for periods of 3000 h. Given the previous study showing that TP^+ is accommodated inside the zeolite supercages,[14] a reasonable explanation is based on molecular modeling.[15] These calculations show that nucleophilic attack to the 2 or 4 position of the pyrylium ring would force the phenyl substituent attached to this carbon to move out of the ring plane (Scheme 2). This would increase the molecular size of TP^+ and would be impeded by the walls of the zeolite cage that rigidly holds the molecular conformation of TP^+. Importantly, to confirm the role played by the TP^+ confinement in the zeolite cages, TPT was deposited in the external surface of amorphous silica (neither micropores nor internal cages), and the resulting $TPT{\cdot}SiO_2$ sample was stirred in water. Although somewhat slower than for unsupported TPT,

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(9) LFP were conducted using a dynamic flow system mixing an acetonitrile TPT solution and water (1:1) 10 s before laser excitation. Controls by using UV/vis absorption spectroscopy showed that TP^+ was unchanged just before the LFP experiment.

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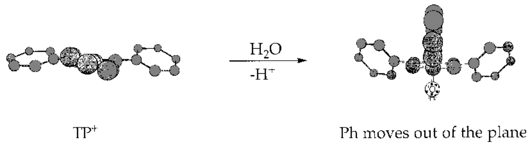
S0002-7863(98)00121-8 CCC: $15.00

Scheme 2



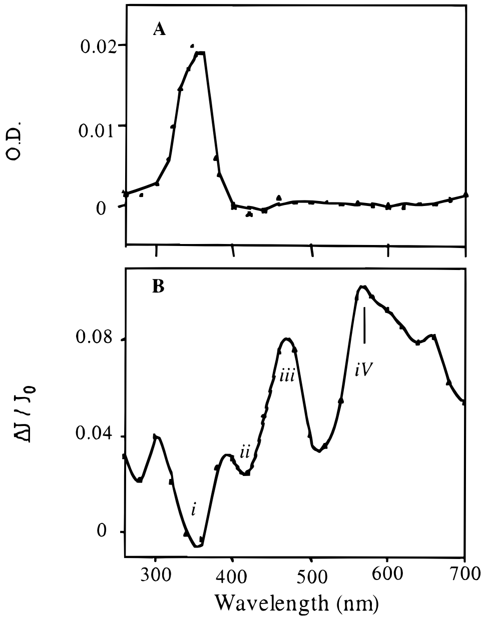


Figure 2. (A) Transient absorption spectrum of a H_2O-saturated solution of TPT in benzene recorded 2 μs after 355 nm laser excitation. (B) Transient diffuse reflectance spectrum recorded 10 μs after 355 laser excitation of a MV^{2+}-doped TPY/H_2O slurry: i and ii correspond to the bleaching of TP^+ ground state, iii is assigned to the $MV^{2+}-OH^•$ adduct, and iv is the absorption of the $TP^•$.

the hydrolysis of TP^+ was complete within a few hours, thus supporting the importance of the spatial confinement.

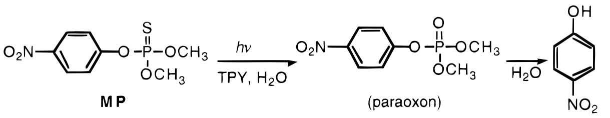
In contrast to the behavior of TPT in acetonitrile/water solutions, LFP of a slurry of TPY in H_2O affords $TP^•$ as a transient species, thus indicating that a PET process occurs when TP^+ is entrapped in the polar zeolite pores (Figure 1B). The ability of zeolites to favor electron-transfer processes is well documented in the literature.[16] As previously reported by us, only TP^+ triplet excited state is observed when TPY is irradiated in the absence of water.[17] To probe whether the primary PET process generating $H_2O^{+•}$ leads to the formation of $OH^•$ radicals, we undertook time-resolved experiments and exploratory product studies.

Thus, a TPY sample, partially dehydrated by heating it at 100 °C under reduced pressure for 1 h, was stirred in neat benzene for 30 min. The suspension was filtered and dried in air. LFP (λ 355 nm, exclusive excitation of TP^+) of this benzene-impregnated TPY in the presence of H_2O leads to the observation of the hydroxycyclohexadienyl radical as a transient characterized by an intense absorption at 350 nm.[18] The same transient spectrum is obtained for a water-saturated TPT solution in benzene (Figure 2A). Likewise, generation of $OH^•$ in the photolysis of TPY in the presence of water was probed by using methyl viologen (MV^{2+}). The adduct resulting of the attack of $OH^•$ to MV^{2+} exhibits an absorption band centered at 470 nm.[19] MV^{2+}-doped TPY was obtained by submitting TPY to ion exchange with an aqueous solution of $MVCl_2$. LFP of MV^{2+}/TPY slurry in water has a band to 470 nm decaying in the microsecond time scale, together with an additional broad band at 570 nm exhibiting a much longer lifetime (Figure 2B). Comparison with Figure 1B indicates that this 570 nm band corresponds, at least in part, to $TP^•$.

The generation of $OH^•$ radicals in the photolysis of TPY in CH_3CN/H_2O (50/50) has also been confirmed in two alternative ways. Irradiation of TPY in the presence of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) generated an EPR signal at $g = 1.997$ compatible with the $[DMPO-OH]^•$ adduct.[20] On the preparative scale, irradiation of benzhydrol (10^{-2} M) in the presence of TPY formed benzophenone (26%) as the sole product.

The potential of TP^+ to generate $OH^•$ radicals has been exploited in the photochemical hydroxylation of benzene. Thus, conventional Hg lamp irradiation (λ 350 nm, 2 h) of TPY in benzene containing water (10 mL of dry benzene with 10 μL of H_2O added with a syringe) leads to the formation of phenol as the predominant product (purity 82% of the 8 mg residue).

Another straightforward application of this TPY/H_2O photocatalytic system is the degradation of pesticides in water. Methylparathion (MP) was chosen because its E_{ox} (2.6 V vs SCE) is high enough to ensure that no direct PET between TP^+ singlet excited state and MP can occur. As a matter of fact, only TP^+ triplet excited state is observed as a transient in the LFP (λ 355 nm, exclusive excitation of TP^+) of a solution of TPT and MP in acetonitrile. In contrast, heterogeneous irradiation of an aqueous suspension of MP using TPY as photosensitizer causes degradation to paraoxon and 4-nitrophenol (eq 1). The kinetics of formation of 4-nitrophenol shows that it is a secondary product and probably arises from hydrolysis of paraoxon. Diffuse reflectance spectroscopy reveals that the TP^+ ion remains unaltered and that TP^+ inside Y zeolite is also protected from the attack of $OH^•$. Further, iodimetric titrations of a lamp irradiated suspension of TPY (300 mg) in distilled water (25 mL) established that the photocatalytic system had generated a stationary concentration of 2.2×10^{-2} M of hydrogen peroxide. H_2O_2, presumably arising from $OH^•$ coupling, is the obvious final product when these radicals do not have alternate reaction pathways. Formation of H_2O_2 in the γ-radiolysis of H_2O (the cleanest way to produce $OH^•$) is well established in the literature.[21] The crystal structure of the zeolite is not damaged in the process as determined by XRD.



(1)

In conclusion, by encapsulation inside the rigid zeolite lattice TP^+ is efficiently protects TP^+ from attack of H_2O or $OH^•$. Upon photolysis of an aqueous slurry of TPY, PET with formation of $TP^•$ pyrylium radical and $OH^•$ occurs. These hydroxyl radicals have been trapped with DMPO and positively detected by time-resolved spectroscopy using benzene and MV^{2+} as probes.

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