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Modification of the Photochemical Reactivity of α,β-Diacetoxystilbene by Adsorption onto a Fe^{3+}-Doped Sepiolite: Comparison with the Direct and 2,4,6-Triphenylpyrylium-Sensitized Photolyses

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Abstract: Photolysis of α,β-diacetoxystilbene (**1**) adsorbed onto a Fe^{3+}-doped sepiolite (Fe-Sp) leads to benzoic acid (**3**), 9,10-diacetoxyphenanthrene (**5**), diphenic anhydride (**6**), and benzil (**7**). While compounds **3**, **5** and **6** are also observed in the direct irradiation of **1** in hexane solution, diketone **7** is formed under electron transfer conditions using 2,4,6-triphenylpyrylium tetrafluoroborate as photosensitizer. These results strongly suggest that formation of benzil (**7**) in the photolysis of **1** on Fe-Sp involves the intermediacy of $\mathbf{1}^{+\bullet}$, generated by single electron transfer from excited **1** to the iron active sites of the clay. In contrast to the unsubstituted stilbene, reactivity of $\mathbf{1}^{+\bullet}$ with ground state molecular oxygen has been established by cyclic voltammetry through the current intensity decrease of the oxidation peak of **1** in the presence of oxygen. Finally, the thermodynamic feasibility of a direct electron transfer pathway between excited $\mathbf{1}^{*}$ and oxygen leading to the formation of a dioxetane intermediate is discussed.

INTRODUCTION

By means of either time-resolved techniques[1-5] or product studies,[6-9] it has been well established that the interaction of organic molecules with surface active sites of microporous or layered solids can alter the course of a photochemical reaction, providing alternative pathways not occurring in homogeneous environments. In this context, many studies have been devoted to systems experiencing acid-base (Brönsted or Lewis) interaction. By contrast, less is known about the oxidizing ability of surfaces and, in particular, the generation of radical cations of electron-rich compounds, through photoinduced single electron transfer.[10-14]

We have provided some examples in which iron-doped sepiolite (Fe-Sp) exhibits a dual behavior as Lewis acid for thermal ground-state reactions or single electron acceptor for excited-state reactions.[15,16] Sepiolite is a natural magnesium aluminosilicate of the talc family, which can be modified by exchanging some of the Mg located at the edge of the fibers by other mono-, di- or trivalent cations, such as Na, Cu or Fe. Owing to the ubiquitous presence of these types of minerals in soils, irradiation of organic compounds onto wellcharacterized Fe-Sp samples can be considered as a simple model to understand the fate of organics in the environment under solar light irradiation.

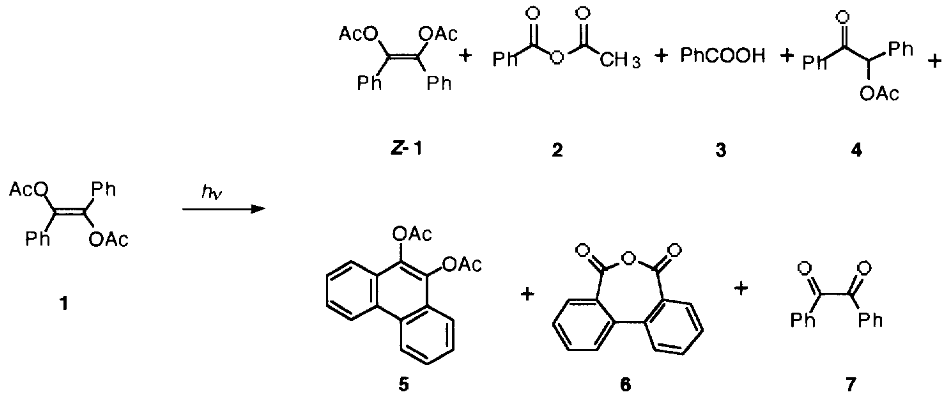
In the present work, we have performed the irradiation of α,β-diacetoxystilbene (**1**) adsorbed onto Fe-Sp. Comparison of these results with those of the direct and electron transfer-sensitized photolyses has shown that interaction of $\mathbf{1}^*$ with the active sites of Fe-Sp leads to the radical cation of $\mathbf{1}^{+\bullet}$, which is trapped by molecular oxygen to afford benzil (**7**)

RESULTS AND DISCUSSION

Owing to the small ion exchange capability of natural samples, Fe-Sp was obtained from an intermediate Na-Sp sample, which was in turn prepared from natural sepiolite by hydrothermal treatment with NaOH.[17-19] The X-ray diffraction pattern of Fe-Sp was identical to that of the original sepiolite. This indicates that the incorporation of Fe did not cause any damage in the crystalline structure of the aluminosilicate. The iron content of Fe-Sp was determined by chemical analysis, while the octahedrical coordination of Fe was established by Mössbauer spectroscopy.

Deposition of **1** onto Fe-Sp was accomplished from CH_2Cl_2 solutions by slow removal of the solvent at room temperature. Exhaustive solid-liquid extraction lead to a complete recovery of unaltered starting stilbene **1**. Attempts to adsorb **1** onto Fe-Sp by allowing the free diffusion of the guest from a solution onto the solid did not result in any appreciable incorporation. These facts would suggest that only the external surface would be accessible to the guest, which would only experience a loose interaction with the surface sites.

Photolysis of **1** onto Fe-Sp was performed in the absence of solvent, in the open air. After irradiation the solid was submitted to continuous extraction. The products observed and their yields are contained in Table 1 and Scheme 1. Although appreciable amounts of benzoic acid were obtained after extraction of the solid, the possibility that an additional portion of this acid **3** could be more strongly adsorbed onto Fe-Sp, and hence non-recoverable by extraction, cannot be ruled out.



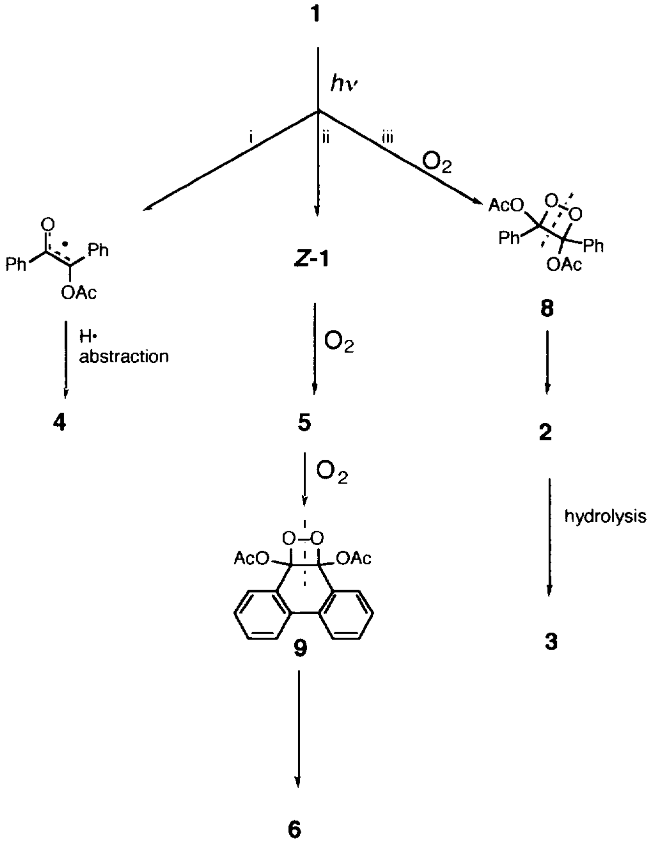
Scheme 1

For comparison direct irradiation of **1** was carried out in homogeneous hexane solutions (Table 1). Under inert atmosphere, the only process observed was *trans-cis* isomerization of the double bond, to give *Z*-**1**.

Table 1. Results of the photolysis of diacetoxystilbene **1** under different conditions.

Conditions[a]	Product Distribution[b] (%)						
	***Z*-1**	**2**	**3**	**4**	**5**	**6**	**7**
Fe-Sp, O_2[c]	--	--	21	--	31	7	22
I, O_2	--	8	30	3	46	5	--
I, Ar[c]	43	--	--	--	--	--	--
TPT, O_2[d]	--	--	36	--	--	--	52

[a] I: Homogeneous irradiation in hexane solution (10^{-2} M). [b] Product formed divided by initial amount of **1** (mol/mol$_0$ x 100).
[c] Unreacted starting material **1** was also present in the reaction mixture. [d] Benzaldehyde was also present.



Scheme 2

Conversely, in the presence of oxygen a complex mixture containing compounds **2**-**6** was obtained. The latter results can be rationalized according to Scheme 2, which involves three main pathways: i, homolytic CO-O bond breaking of the of the enol ester moiety followed by hydrogen abstraction; ii, oxidative electrocyclic ring closure after initial C=C double bond isomerization; iii, degradative photooxygenation of the C=C double bond.

Routes i and ii are generally observed in the photolysis of organic substrates comprising α-aryl substituted enol esters[20-23] and stilbene[24,25] substructures, respectively. It is worth mentioning that 9,10-phenanthrenediol is a useful synthetic intermediate,[26-28] which can be obtained by the photocyclization of stilbenediol carbonates[27,29,30] and borates.[31] The direct photolysis of **1** also allows the access to this type of phenanthrene derivatives with preparative yields similar to those previously reported, while avoiding the use of highly toxic reagents such as phosgene[29,30] or selenides.[31]

Concerning the oxidative C=C bond cleavage (pathway iii), benzoic acid (**3**) would arise from dioxetane **8**. This is firmly supported by detection of the mixed anhydride **2**, which would be the direct product of the cycloreversion of **8**. Analogous oxygenation of phenanthrene **5** would explain the appearance of diphenic anhydride **6**.

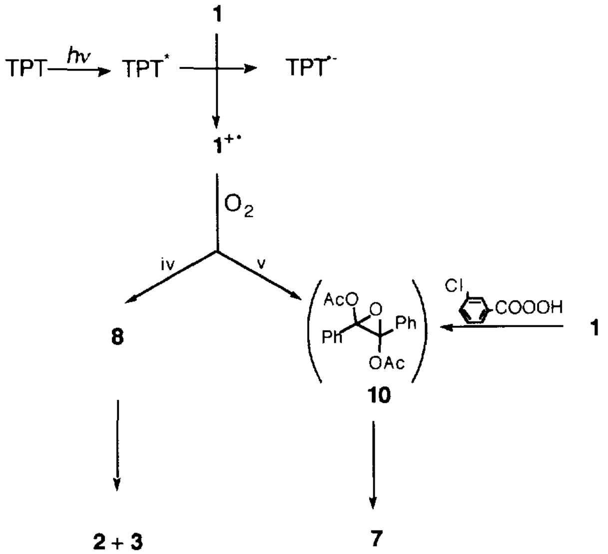
In this context, the closely related cycloreversion of dioxetane intermediates leading to benzoic esters in the series of 2,3-diaryl-1,4-dioxenes (cyclic ethyleneglycol ethers of α,β-stilbenediol) has attracted much attention.[32-37] It has been established that dioxetanes may arise from the reaction of singlet oxygen with the C=C double bond. However, in the case of the direct irradiation of **1**, the absence of any typical photosensitizer makes unlikely the efficient generation of $^1O_2$. An alternative reaction mechanism to account for dioxetane **8** would consist of electron transfer between excited **1*** and molecular oxygen to give $\mathbf{1}^{+\bullet}$ and $O_2^{-\bullet}$ (eq. 1). This route has already been proposed for the 1,4-dioxene analogues.[37] In fact, generation of superoxide in the direct irradiation of electron-rich alkenes through electron transfer from the organic compound as donor to molecular oxygen as acceptor is widely accepted.[38,39] From a thermodynamic point of view, this mechanism fulfills the requirements of the Rehm-Weller equation.[40] Thus, applying the experimental values for $\Delta E_{0,0}$ of **1** (80 kcal x mol^{-1}, measured from absorption and emission spectra), the redox potentials of $\mathbf{1}^{+\bullet}/\mathbf{1}$ and $^3O_2/O_2^{-\bullet}$ (1.8 and -0.78 v, respectively; measured by cyclic voltammetry) in eq. 2 and neglecting the smaller contribution of the coulombic $e^2/\varepsilon a$ term, a large negative number for free energy change of the electron transfer process is obtained.

$$\mathbf{1}^* + {}^3O_2 \rightarrow \mathbf{1}^{+\bullet} + O_2^{-\bullet} \rightarrow \mathbf{8} \quad [\text{eq. 1}]$$

$$\Delta G = 23.06\,[E(\mathbf{1}^{+\bullet}/\mathbf{1}) - E(O_2/O_2^{-\bullet}) - e^2/\varepsilon a] - \Delta E_{0,0} = -\,20.5 \text{ kcal x mol}^{-1} \quad [\text{eq. 2}]$$

When comparing the results obtained in the photolyses of **1** adsorbed on Fe-Sp with those in homogeneous phase, a remarkable difference was the lack of benzil **7** under the latter conditions. To establish the possible origin of this diketone, photolysis (λ>400 nm) of **1** in CH_2Cl_2 solution was carried out in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT). This salt is a well-documented electron transfer photosensitizer,[41] whose photooxygenations are known to be free from adventitious singlet oxygen or superoxide formation.[41-43] In the case of TPT-mediated photolysis of **1** (Table 1), benzil **7** was the predominant product, accompanied with benzoic acid.

In fact, in the case of 2,3-diphenyl-1,4-dioxene analogues of diacetate **1** the same type of products (benzil plus benzoates) are obtained under electron transfer conditions. Moreover, it has been established that these products arise from different intermediates, benzil being the characteristic product derived from the radical cation.[35,37,44] Comparison of the results of Table 1 in the absence and presence of TPT indicates that the same is true for diacetate **1**.



Scheme 3

According to Scheme 3, we addressed the possibility that $1^{+\bullet}$ could react directly with molecular oxygen. It has been proposed that variations on the current intensity of oxidation peaks in cyclic voltammetry is a simple diagnostic tool to assess the reactivity of radical cations with O_2.[45,46] In fact, based on the absence of current changes in the cyclic voltagram, it was concluded that stilbene radical cation does not react with O_2, albeit radical cations of closely related derivatives do undergo reaction.[45] We have recorded the cyclic voltagrams of compound 1 (Figure 1) and we have observed a significant decrease on the current intensity of the oxidation peak when O_2 is present. This has been ascribed to the occurence of a chemical reaction, thus suppressing the subsequent anodic oxidation of the electrogenerated radical cation.

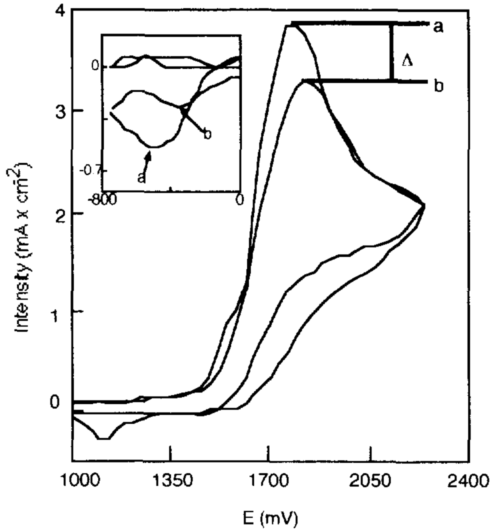
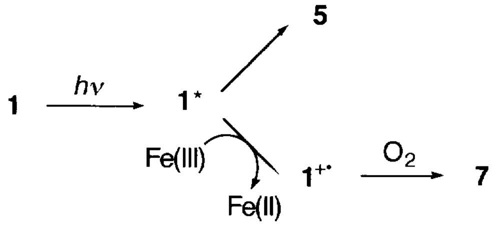


Figure 1. Oxidation peaks of the cyclic voltagrams (scan rate 100 mV x s^{-1}) of 1 in dry acetonitrile using tetra-n-butylammonium tetrafluoroborate as supporting salt under Ar (a) and under O_2 (b). The current intensity maxima measured under the same conditions were 3.868 and 3.303 mA x cm^{-2} for voltagrams a and b, respectively. The resulting current ratio (Ar/O_2) of the oxidation peaks and was 1.17. The inset shows the differences observed in the reduction part of the cyclic voltagrams



Scheme 4

We have shown that oxirane intermediates are generally involved in the photooxygenation of aryl olefins using TPT.[41,47-49] In order to get some support to the intermediacy of oxirane **10** in the formation of benzil (**7**) (pathway v of Scheme 3), we performed the epoxidation of **1** with *m*-chloroperbenzoic acid. As anticipated, the only product that could be detected was benzil (**7**).[50]

In conclusion, we have found that irradiation of diacetoxystilbene **1** adsorbed onto an iron-doped sepiolite leads to a product distribution containing phenanthrene derivatives such as **5** and **6**, characteristics of the direct irradiation, together with benzil (**7**), typically derived from the radical cation $\mathbf{1}^{+\bullet}$. We propose (Scheme 4) that after light absorption, $\mathbf{1}^{+\bullet}$ would be generated through the interaction of $\mathbf{1}^*$ with the active sites of the solid surface. Our report constitutes an interesting example of the "active role"[51] that solid surfaces may play controlling the photochemistry of organic adsorbates.

EXPERIMENTAL

α,β-Diacetoxystilbene (**1**) was readily prepared in excellent yields by reductive acetylation of benzil with acetic anhydride and hydrochloric acid.[52] Recrystallization from ethanol afforded the pure *E* stereoisomer. TPT was a commercial sample (Aldrich) and used as received. Fe-Sp was obtained by treating a natural sepiolite sample (Vallecas, Spain) with aqueous solution of NaOH in autoclave at 110 °C, followed by Fe^{3+}-to-Na^+ exchange using $FeCl_3$. A detailed experimental procedure has been reported elsewhere.[17,18] X-Ray diffraction of Fe-Sp was recorded with a Philips 1710 instrument using the filtered $CuK_{\alpha}Ni$ radiation. Chemical analysis established that the iron content was 1.7 meq x g^{-1}. ^{54}Fe-Mössbauer spectroscopy confirmed the oxidation state of Fe atoms. Diffuse reflectance was performed using a Shimadzu UV-2101 PC scanning spectrophotometer and exhibited a broad absorption band with a maximum at 410 nm. Cyclic voltammetries of **1** were carried out at room temperature under argon or oxygen in a Tacussel potentiometer, using dry acetonitrile as solvent, tetra-n-butylammonium tetrafluoroborate (0.1 mol x l^{-1}) as supporting electrolyte, and a scan rate of 100 mV x s^{-1}.

Direct photolysis of **1** (200 mg, 0.7 mmol) in the presence of oxygen was carried out at room temperature in hexane solution (300 mL) under magnetic stirring, using a quartz immersion well photoreactor provided with a 125 W medium pressure mercury lamp for 2 h. For anaerobic irradiations the solution, previously degassed by argon bubbling, was placed in sealed quartz test-tube and irradiated externally with the same set-up for 2 h. After photolysis, the reaction mixtures were analyzed by GC/MS (HP 5988 A spectrometer fitted with a 25 m capillary column of crosslinked 5% phenylmethylsilicone) and GC/FTIR (HP 5890 cromatograph coupled to a HP 5965 A FTIR detector). Compounds were identified by comparison with autentical samples.

TPT-sensitized photooxygenation of **1** (200 mg, 0.7 mmol) was performed in CH_2Cl_2 (50 mL) containing TPT (40 mg) using a Pyrex photoreactor and an aqueous solution of potassium chromate as filter[53] for 1 h. The reaction work-up was the same as for the homogeneous photolysis.

Adsorption of **1** onto Fe-Sp was accomplished by stirring magnetically at room temperature a suspension of **1** (25 mg, 8.5 x 10^{-2} mmol) in CH_2Cl_2 (30 mL) and Fe-Sp (500 mg) under reduced pressure until all the solvent was evacuated. Continuous extraction using a micro-Soxhlet equipment (10 ml) led to a total recovery of unaltered starting material. Alternatively, the resulting sample was pressed into discs and irradiated externally for 2 h using a 125 W medium pressure mercury lamp placed inside the quartz well, refrigerated by running water. After this time, the discs were extracted with CH_2Cl_2 and the organic phase weighed and analyzed by GC-MS and GC-FTIR.

Epoxidation of **1** (50 mg, 0.17 mmol) with *m*-chloroperbenzoic acid (30 mg, 1.9 mmol) was carried out in CH_2Cl_2 at -20 ^{o}C for 3 h. After this time, the reaction mixture was allowed to stand at room temperature. Besides unreacted starting material (78 %), analysis by GC established the formation of benzil (20 %) as the only product.

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