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Dual behaviour of sepiolites as single electron acceptors or Lewis acids: reactivity of two α-acetoxystyrenes adsorbed on a iron(III)-exchanged sepiolite

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Abstract. Iron(III)-exchanged sepiolites exhibit dual behaviour as catalysts in the reactions of α-acetoxystyrenes **1a,b**; operating as Lewis acids (to give **2–5**) in thermolysis reactions under reduced pressure or as single-electron acceptors (to give **7**) in photolysis under aerobic conditions.

Introduction

Due to their adsorption properties, their large available surface area and their ability to be modified by ion exchange, clays[1] are among the most versatile materials with which to perform studies on the chemical reactivity of organic compounds in dry media. The interaction of solid active sites with substrates can influence the operating mechanism, determine product distribution and make it possible to achieve a selectivity different from homogeneous liquid-phase reactions.

The reaction of α-acetoxystyrene (**1a**) catalyzed by BF_3 has been reported to yield the 1,3-acetyl migration product **3** together with acetophenone (**2a**), arising from partial acid hydrolysis of the enol ester[2]. No data are available concerning the behaviour of the *o*-acetoxy derivative **1b** under analogous conditions.

On the other hand, the photochemistry of compounds **1a,b** in solution under aerated conditions has been investigated[3,4]. The most salient features found were 1,3-acetyl migration of **1a** to **3** and intramolecular photocyclization of **1b** to give compound **4** with a γ-pyrone ring.

The present paper is concerned with the different patterns observed in thermal and photochemical reactivity of α-acetoxystyrenes **1a,b** adsorbed on an iron(III)-exchanged sepiolite (Fe-Sp), which can be attributed to the ability of the sepiolite metal sites to act either as Lewis acids or as oxidizing reagents.

Results and discussion

Modified sepiolite Fe-sp was prepared by heating natural samples with aqueous sodium hydroxide at 110°C and submitting the Na-Sp clay to further exchange with ferric chloride solution. The resulting material contained 1.7 meq/g of Fe^{3+} on the border of the octahedral layers of the fibers and hence accessible from the cavities.

Acetoxystyrenes **1a,b** were prepared from acetophenone and *o*-acetoxyacetophenone by acetylation of their respective enols using isopropenyl acetate. Adsorption on Fe-Sp was accomplished by stirring a suspension of **1** in isooctane and the clay at room temperature.

The results obtained after thermolysis and photolysis of **1a,b** under these conditions are summarized in Table I. The reactions of compounds **1a,b** under photosensitization by 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) were also investigated and the results are included in Table I.

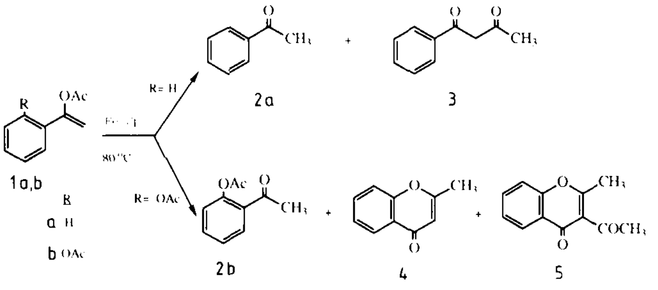
Table I Reactivity of **1a,b**,

Substrate	Reaction conditions[a]	Recovered starting material (%)	Products (%)
1a	I	47	**2a**(36), **3**(3)
	II	16	**7a**(58)
	III	–	**2a**(9), **7a**(83)
1b	I	62	**2b**(8), **5**(2), **4**(10)
	II	28	**7b**(49)
	III	–	**2b**(17), **7b**(76)

[a] I: thermolysis at 80°C adsorbed on Fe-Sp; II: photolysis adsorbed on Fe-Sp; II: TPT-photosensitization. [b] *o*-Hydroxyacetophenone was also detected.

Thermolysis of enol acetates **1** gives products of hydrolysis (**2a**, **2b**) 1,3-acetyl migration (**3**) or cyclodensation (**4**, **5**) (Scheme 1). All these processes can be rationalized by assuming that the active sites of the sepiolite act as acid centers.

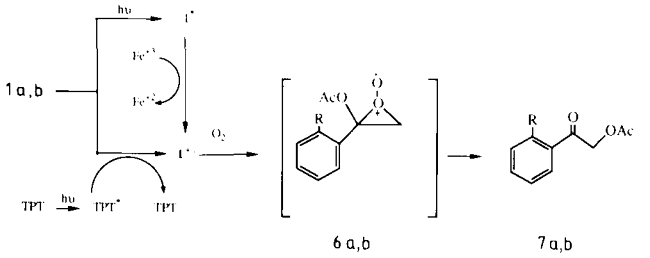
In fact, the active sites of the Fe-Sp clay exhibit moderate acidity, as has been established by FT-IR spectroscopy of pyridinium ions remaining on the Fe-Sp after treatment with pyridine vapors and subsequent evacuation at 180°C and 10^{-4} Torr[5]. Moreover, this activity must be exclusively ascribed to the introduced Fe^{3+}, because the original natural samples do not retain any pyridine under the same experimental conditions.



Scheme 1. Products of the thermolysis of **1a,b** *adsorbed on Fe-Sp.*

On the other hand, in the photolysis of **1a,b** adsorbed on Fe-Sp, the actual products were **7a** and **7b**, whose formation involves oxidation of the enol double bond. In this case, it is obvious that the mild oxidizing nature of the transition metal ions introduced on the clay surface should play an important role. In fact, it has been reported that Fe^{3+} acts as a single electron acceptor for aromatic olefins[6] and that related clays can generate the radical cation of styrene[7]. As a matter of fact, we were able to detect by ESR the radical cation of perylene when this aromatic hydrocarbon, used as a standard mechanistic probe, was adsorbed on the Fe-Sp clay. Moreover, the photolysis of **1a,b** in CH_2Cl_2 solution using TPT, a well-established single-electron-transfer photosensitizer[8-10], gave rise to the same products (**7a**, **7b**) obtained in the Fe-Sp experiments. These were, in addition, completely different to those reported as arising from direct photolysis of **1a,b**[3,4].

Based on these data, the most likely mechanism (Scheme 2) involves single electron transfer from the excited α-acetoxystyrenes to Fe^{3+} to give, together with Fe^{2+}, the radical cations **1**$^{+\cdot}$. These intermediates would react with oxygen and, although we do not have conclusive evidence at present, a perepoxide-like species **6** appears to be a reasonable intermediate in the pathway leading to **7**.



Scheme 2. Proposed mechanism for the photolysis of **1a,b** *adsorbed on Fe-Sp and sensitized by TPT.*

In summary, we have found that adsorption on a iron(III)-exchanged sepiolite modifies the reactivity of α-acetoxystyrenes **1** and that the active centers can act as Lewis acids or oxidizing sites.

Experimental

Fe-Sp

The Fe^{3+}-exchanged sepiolite was prepared by treating natural samples from Vallecas (Spain) with aqueous 1M NaOH in a 1-to-4 solid-to-liquid ratio (w/w) at 110°C in an autoclave for 2 h. The resulting solid was thoroughly washed with distilled water and stirred at room temperature with an aqueous solution 0.5M $FeCl_3$ for 3 h. The Fe-Sp sample was finally dried at 100°C for 5 h. Chemical analysis of the resultant Fe-Sp established that the Fe content was 1.7 meq/g. while the oxidation state was confirmed by ^{54}Fe Mössbauer spectroscopy.

X-Ray diffraction patterns were obtained using a Philips 1710 diffractometer using CuKαNi-filtered radiation. These showed that the new materials have the same channel structure as the original sepiolite. The acidity of the Fe-Sp by pyridine adsorption was measured in a Perkin–Elmer 580 B spectrometer equipped with a data station[5]. The perylene radical cation was detected by recording the EPR spectrum of a sample of the polycyclic aromatic compounds adsorbed on the Fe-Sp inside the probe of a Brucker 200 Spectrometer at 77 K.

Organic substrates

α-Acetoxystyrenes **1a,b** were obtained by heating at about 90°C acetophenone of *o*-acetoxyacetophenone (5 mmol) with isopropenyl acetate (20 ml) and *p*-toluenesulfonic acid (200 mg) while continuously removing the resulting acetone by distillation, as described by *Garcia* et al.[11].

TPT was prepared by condensation of chalcone (1,3-diphenyl-2-propen-1-one) (2.08 g, 10 mmol) with acetophenone (1.20 g, 10 mmol) in 1,2-dichloroethane (350 ml) using a 50% ethereal solution of tetrafluoroboric acid (160 ml) at 70°C, following the procedure of *Climent* et al.[12].

Reaction procedures

Fe-Sp (1.00 g) was activated by heating at about 150°C under 1 Torr for 3 h prior to use. Adsorption was performed by pouring under reduced pressure a solution of the corresponding α-acetoxystyrene **1** (0.50 g) in isooctane (50 ml) on to the sepiolite and stirring the resulting suspension at room temperature for 1 h. The solid was then filtered, washed with fresh solvent and dried under reduced pressure. The adsorbed weigh of **1** was calculated from the difference between the initial 0.5 g and the recovered amount from the organic solutions.

Thermal reactions were carried out by heating at 80°C under reduced pressure for 4 h. Photolysis was performed in the open air at 25°C for 4 h, using a 125-W medium-pressure mercury lamp provided with a Pyrex filter. Organic compounds were recovered by continuous extraction using a 10-ml micro-Soxhlet apparatus and CH_2Cl_2 as solvent, until the organic material accounted for more than 90% of the initial amount. TPT-sensitized photolysis of **1** (0.5 g) was accomplished at 10°C in CH_2Cl_2 solution (300 ml) in the presence of catalytic amounts of TPT (40 mg) inside a Pyrex immersion-well photoreactor using aqueous K_2CrO_4 solution (100 mg/ml) as filter.

The reaction mixtures were analyzed by GC-MS (Hewlett-Packard 5988 A spectrometer) and GC-FTIR (Hewlett-Packard 5890 GC coupled with a 5965 A FT-IR detector) provided with a 25-m capillary column of cross-linked 5% phenyl methyl silicone. The structures of the products were confirmed by comparison with authentic samples.

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