Photochemistry of phenyl phenylacetates adsorbed on pentasil and faujasite zeolites

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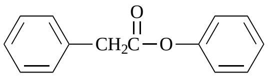
The photochemistry of phenyl phenylacetate 1, *p*-tolyl phenylacetate 2, *o*-tolyl phenylacetate 3 and phenyl *o*-tolylacetate 4 was investigated both in homogeneous solution and adsorbed on ZSM-5 and NaY zeolites. Photolyses of these esters in acetonitrile result in photo-Fries rearrangement products, phenols and diphenylethane as well as phenyl benzyl ethers. In contrast, photolyses of these esters adsorbed on NaY zeolite only give the *ortho* Fries rearrangement products. On the other hand, the photochemical reaction of 1 and 2 adsorbed on ZSM-5 zeolite only produces toluene and phenols, while under identical conditions the photochemical products for 3 and 4 are the Fries rearrangement and decarbonylation products. The product distributions for these esters adsorbed both on ZSM-5 and NaY zeolites are different from those for dibenzyl ketones as reported in the literature. All of these observations are interpreted in terms of (*a*) the size and shape sorption selectivity of ZSM-5 zeolite, (*b*) restriction of diffusional and rotational mobility of the radical pair imposed by the zeolite surface and (*c*) the multiplicity of the excited state responsible for the homolytic bond cleavage.

Introduction

The photochemical reactions of organic molecules included in zeolites usually show some deviation of product distribution from their solution reactions and in some cases result in the occurrence of reaction pathways that are not otherwise observed.[1] These effects are attributed to size and shape sorption selectivities combined with restriction on rotational and translational motion of adsorbed molecules and intermediates imposed by the zeolite internal and/or external surfaces.[2] Among the many classes of zeolites used in photochemical studies, the pentasil and faujasite family of zeolites are two outstanding members. The internal surface of ZSM-5, a member of the pentasil family, consists of two types of pore systems (channels):[3] one is sinusoidal with a nearly circular cross section of *ca.* 5.5 Å, and the other is straight and perpendicular to the sinusoidal channels. The straight channels are roughly elliptical with dimensions of *ca.* 5.2 × 5.8 Å. The structure of the faujasite family consists of an interconnected three-dimensional network of relatively large spherical cavities, termed supercages, with a diameter of *ca.* 13 Å.[3] Each cage is connected tetrahedrally to four other supercages through 8 Å windows or pores.

Although much progress has been made in the use of zeolites as constrained and ordered media to gain selectivity in organic phototransformations over the past couple of decades, it is still not particularly easy to predict the extent and direction of the effect of the zeolite surfaces on the photochemical reactions of adsorbed molecules in any given case. Thus, additional experiments are obviously required to understand the complex range of factors that control the behaviour of the adsorbed species. Furthermore, although the chemistry of triplet radical pairs on zeolites has been well investigated, relatively little has been reported on the chemistry of singlet radical pairs adsorbed on zeolites.[1] In the present paper we will address the following questions: (*a*) How do the size and shape of channels and/or supercages of ZSM-5 and NaY zeolites control the location of the included guest molecules? (*b*) How do the surfaces of these two zeolites restrict the transportation and rotation of the radicals photochemically generated in their framework? (*c*) What is the difference in the chemistry between triplet and singlet radical pairs on zeolites? We have studied the photochemistry of phenyl phenylacetate **1**, *p*-tolyl phenylacetate **2**, *o*-tolyl phenylacetate **3** and phenyl *o*-tolylacetate **4**, adsorbed in ZSM-5 and NaY zeolites. We expect that these esters would be appropriate photochemical probes for investigating the effects of zeolite surfaces on radical reactions. First, **1** and **2** possess a different size and shape from that of **3** and **4**. Thus, they should show size and shape sorption selectivities upon adsorption on zeolites, particularly on ZSM-5. Secondly, the product distributions for the photochemical reactions of **1**–**4** would probe the restriction on rotational and translational motions of the radical intermediates imposed by zeolite surfaces, as described below.



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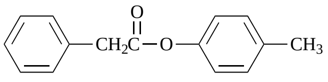

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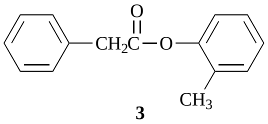

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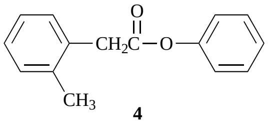

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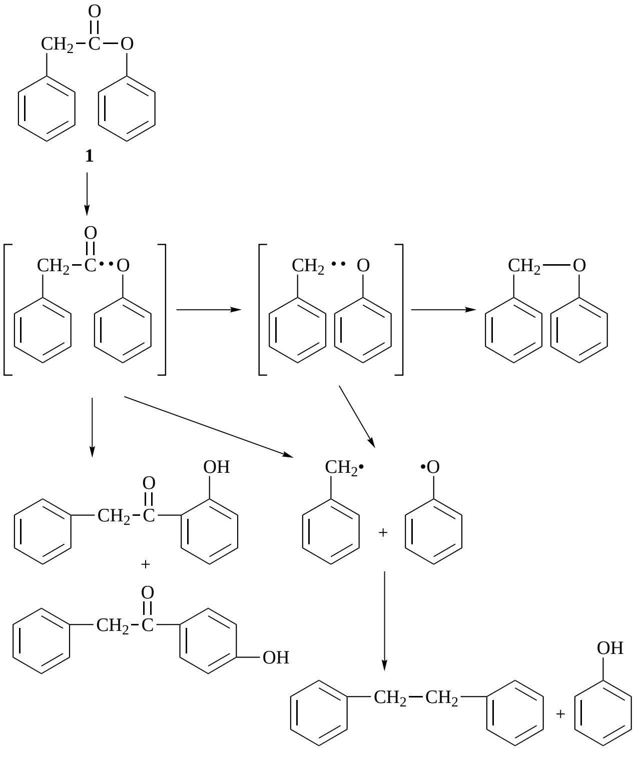
The photochemistry of esters **1**–**4** is expected to be analogous to that of phenyl acetate whose photochemistry in homogeneous solution has been well investigated.[4] Scheme 1 shows the photochemical reactions of these esters with **1** as the example. Upon photoirradiation, **1** undergoes C–O bond homolytic cleavage to give two paired radicals (termed a primary geminate radical pair). The solvent molecules create a 'cage' surrounding the radical pair. This geminate radical pair in the cage recombines to form the starting ester or *o*- and *p*-hydroxyphenones. The latter reaction is known as the photo-Fries rearrangement. The phenylacetyl radical may undergo decarbonylation in the cage to produce the secondary radical pair which in turn produces phenyl benzyl ether. Thus, the hydroxyphenones and phenyl benzyl ether may be viewed as 'cage' products. The radical pair may also undergo diffusive separation to give free phenoxyl and phenylacetyl radicals. The active phenoxyl radical would easily abstract a hydrogen atom to form phenol. The phenylacetyl radical can be expected to decarbonylate generating a benzyl radical which in turn under-

Table 1 The production distribution of esters[a] **1–4**

Substrate	Medium	Phenol	Toluene	Ether[b]	Diphenyl-ethane	*ortho*[c]	*para*[d]	Cage effect	*ortho*/*para*
1	Acetonitrile	4.8	0	0	4.7	66.4	24.3	90.7	2.73
	ZSM-5	70.9	100	0	0	0	0	100	—
	NaY	0	0	0	0	100	0	100	∞
2	Acetonitrile	6.8	0	3.3	8.5	79.7	—	91.5	—
	ZSM-5	73.0	100	0	0	0	—	100	—
	NaY	0	0	0	0	100	—	100	—
3	Acetonitrile	2.53	0	3.5	12.0	55.2	17.4	76.1	3.17
	ZSM-5	10	0	7	2.5	79	9	95	8.78
	NaY	0	0	0	0	100	0	100	∞
4	Acetonitrile	8.2	0	8.6	15.2	40.2	20.7	69.5	1.94
	ZSM-5	0	0	12.7	10.3	54.0	12.7	79.4	4.25
	NaY	0	0	0	0	100	0	100	∞

[a] Molar ratio, error limit ± 2%. [b] Phenyl benzyl ether. [c] *ortho* rearrangement product. [d] *para* rearrangement product.



Scheme 1

goes self-coupling to yield diphenylethane. Thus, phenol and diphenylethane are the 'escape' products. The cage effect is defined as the fraction of the yields of hydroxy phenones and phenyl benzyl ether in the total yield of all of the products. Restriction on the diffusion of the radicals would increase the cage effect. Suppression of the rotation of the radicals would decrease the yield of the photo-Fries rearrangement products and enhance the ratio of the *o*-hydroxyphenone to the *p*-hydroxyphenone, since formation of a *para* rearrangement product requires a greater extent of the rotation of the radical than in the formation of an *ortho* product. Thus, one can use the cage effect and the ratio of *o*- to *p*-hydroxyphenone as probes for investigating the diffusibility and rotational mobility of radicals, respectively, in confined media. Furthermore, the bond cleavage of **1**–**4** has been established to be from their singlet excited state, resulting in a singlet radical pair.[4,5] The chemistry of triplet radical pairs produced by photolyses of ketones on zeolites has been well studied.[1] Thus, comparison of the photochemistry of **1**–**4** on zeolites with that of ketones may give an insight into the role played by the multiplicity of the radical pair in its chemistry. We found that the product distributions for photolyses of esters **1**–**4** on pentasil and faujasite zeolites indeed provide valuable information on size/shape sorption selectivity and on the extent of restriction of the radical motions offered by the zeolite surfaces as well as on the role of the multiplicity of the radical pair in its chemistry performed on zeolites.

Results

Photolysis in homogeneous solutions

Photoirradiation of esters **1**–**4** with a medium-pressure mercury lamp in deoxygenated acetonitrile solution leads to the formation of *para* and *ortho* rearrangement products, benzyl phenyl ethers, phenols and 1,2-diphenylethanes as shown in Scheme 1. For all four substrates, the total yields of the isolated products are greater than 90% based on the consumption of the starting materials and the main products are the *o*-hydroxyphenones (Table 1). In Table 1 the percentage cage effects and the ratio of *o*- to *p*-hydroxyphenones in the Fries rearrangement products are also given.

Photolysis on ZSM-5 zeolites

The esters were deposited on the zeolites by mixing a solution of the esters in CH_2Cl_2 with a pre-weighed amount of activated zeolites at room temperature followed by evaporation of the solvent. In all cases, the loading level was kept low, usually *ca.* 1 mg of esters per 100 mg of zeolite. The samples were degassed under vacuum and photolysed. After photolysis, samples were extracted with CH_2Cl_2 and mass balances of *ca.* 70–80% were achieved in all cases reported and appear to be limited by the extent of extraction. However, the product ratios were independent of the extent of extraction, except for the phenols. For complete removal of the phenols from ZSM-5 zeolite longer extraction times are needed.

Product distributions for photolyses of esters **1**–**4** on ZSM-5 zeolite are listed in Table 1. Surprisingly, the photolyses of **1** and **2** adsorbed on ZSM-5 yield the corresponding phenols and toluene as the only products. The major products—rearrangement products—in homogeneous media are not detected in the photolyses on ZSM-5. Nor were phenyl benzyl ethers detected. In contrast, the photolyses of **3** and **4** adsorbed on ZSM-5 zeolite give both photo-Fries and decarbonylation products. The product distributions are evidently different from those in homogeneous solution (Table 1).

Photolysis on NaY zeolites

The photolysis experiments described above were performed with NaY substituting for ZSM-5. Product distributions of the photochemical reaction of esters **1**–**4** are summarized in Table 1. For all four esters, the only products detected are *ortho*-rearrangement products. We could not detect *p*-hydroxyphenone nor decarbonylation products—phenols, diphenylethanes and phenyl benzyl ethers.

Discussion

Photolysis on ZSM-5 zeolite—size- and shape-selective reactions

For samples photolysed on ZSM-5 zeolite, the product distributions from **1** and **2** are dramatically different from those photolysed in homogeneous solutions. First, the rearrangement products were totally suppressed. Secondly, diphenylethane resulting from coupling of benzyl radicals was not found. Only phenols and toluene were detected. In contrast, photolyses of **3** and **4** on ZSM-5 follow strikingly different pathways. Both photo-Fries rearrangement and decarbonylation products were formed. These results can be understood from consideration of size and shape selective sorption combined with restriction on the mobility of the substrates and reaction intermediates imposed by the pentasil pore system.[6]

An example of the size and shape sorption selectivities of ZSM-5 is provided by the comparison of the diffusivities of xylene isomers in ZSM-5. The diffusivity of *p*-xylene is *ca.* 1000–10 000 times faster than that of either *m*-xylene or of *o*-xylene and this enormous difference is ascribed to the larger size and shape of the *ortho* and *meta* isomers relative to the size and shape of the pore diameter of the ZSM-5 framework channels.[6] The structures of **1** and **2** are similar to *p*-xylene, and they are expected to diffuse into and to be adsorbed within the internal surface of the pentasil. In the pentasil internal channels, **1** and **2** can only adopt a linear conformation to orientate themselves with the long axis of the molecules coinciding with the straight framework channels.

As shown in Scheme 1, the homolytic cleavage of the C–O bond of the excited state of esters results in the production of two paired radicals. The kinetic pore diameter of the ZSM-5 framework channels is *ca.* 6 Å,[3] and the benzene ring has a kinetic diameter of 5.85 Å.[3] Thus, the fit inside the channels would be very tight. Such a tight fit and interaction between the radicals and the surfaces of ZSM-5 would restrict both diffusion and rotational motion of the radicals within the channels of ZSM-5. As observed, restriction on rotational motion of the radicals, which is required for Fries-rearrangement, would inhibit formation of *p*- and *o*-hydroxyphenones. Since diffusional separation of the radicals is also suppressed, only regeneration of the esters (**1** or **2**) and loss of CO would be expected to result from the primary radical pair. Indeed, we found that the efficiency of the photolyses of **1** and **2** in ZSM-5 is lower relative to **3** and **4** under identical irradiation conditions, suggesting that, for **1** and **2**, recombination of the primary radical pair to form the starting materials occurs.

Turro and his co-workers[1g] reported that photolysis of *p*-methylbenzyl benzyl ketone (*p*-ACOB) sorbed on ZSM-5 resulted mainly in the coupling product (*p*-AB) of a benzyl radical (B·) with a *p*-methylbenzyl radical (*p*-A·), and the amounts of *p*-A–*p*-A and BB were very small. They suggested that *p*-ACOB was sorbed in the zeolite framework during photolysis, and the internal surfaces restricted the diffusion of the photochemically generated radicals. Thus, the coupling of the geminate radical pair predominated the radical reactions. In the case of photolysis of **1** or **2** on ZSM-5, no coupling product (benzyl phenyl ether) of the geminate radical pair was detected. This observation might be attributed to the fact that abstraction of a hydrogen atom for the phenoxyl radical to form phenol is faster than its diffusion to access the benzyl radical and mutual coupling, although the two geminate radicals are separated only by a small distance. Since the diffusion of the benzyl radical generated by decarbonylation of the phenylacetyl radical is also seriously inhibited, this radical has enough time to abstract a hydrogen atom before encountering another benzyl radical. Thus, toluene rather than diphenylethane was produced. In this sense, toluene and phenol can be viewed as the 'cage' products. Because toluene and phenol are the unique products, the cage effect is 100%.

In contrast to **1** and **2**, the structures of **3** and **4** resemble *o*-xylene and possess a size/shape which inhibits their diffusion into the ZSM-5 channel system. Thus, they are adsorbed on the external surfaces of ZSM-5. Molecules and intermediates on the external surfaces are expected to experience much less restriction to their diffusional and rotational motion. Therefore, both rearrangement and escape products are expected to be produced. Indeed, photolysis of **3** or **4** adsorbed on ZSM-5 zeolite results in both Fries rearrangement and decarbonylation products. However, close inspection of the product distribution reveals that both the cage effect and the ratio of *o*-hydroxyphenone to *p*-hydroxyphenone for photolysis of **3** or **4** on ZSM-5 are evidently greater than those for photolysis in homogeneous solution. This observation suggests that the external surface of ZSM-5 significantly restricts the diffusional and rotational motions of the photogenerated radicals. It has been established[1d] that *o*-methylbenzyl benzyl ketone (*o*-ACOB) was sorbed only on the exterior surface of dry ZSM-5 zeolite. Photolysis of this ketone would generate the *o*-A· and B· radicals on the external surface of the zeolite, and the smaller B· radical moiety was efficiently sieved into the internal framework of the zeolite. Thus, a high negative cage effect was observed. In the case of photolysis of **3** or **4** adsorbed on the external surface of ZSM-5, the cage effects are highly positive. The difference in cage effects between *o*-ACOB and esters **3** and **4** might originate from the different multiplicity of the reactive states of the ketone and the esters. The reactive excited state of dibenzyl ketone and its derivatives is the triplet state. Homolytic cleavage of the C–C bond from the triplet excited state of *o*-ACOB would yield a triplet primary geminate radical pair. After decarbonylation the triplet radical pair *o*-A· ·B is formed. For recombination, this radical pair has first to undergo intersystem crossing to its singlet state. Thus, the smaller radical moiety has enough time to diffuse into the internal framework of ZSM-5 before it reacts with another radical on the external surface. On the other hand, we have demonstrated by using a magnetic field effect as a probe that the reactive state of esters **1**–**4** is the singlet excited state.[5] Homolytic cleavage of the C–O bond should give a singlet radical pair. This radical pair may immediately undergo combination to produce Fries rearrangement products without intersystem crossing. Thus, the cage effect is positive.

The location of esters **1**–**4** and their photoproducts on ZSM-5 zeolite described above was supported by extraction experiments. The size and shape characteristics of isooctane prevent it from being sorbed into ZSM-5 internal framework,[7] so that it is a selective solvent for extraction of species weakly adsorbed on the external surface of ZSM-5. We found that for **1** and **2** both the substrates and the photochemical products could not be extracted from the zeolite surface by isooctane, suggesting that the substrates and products were included in the zeolite channel system. On the other hand, for **3** and **4** both the starting materials and the products were easily extracted except diphenylethane (for **3**) and phenol (for **4**), suggesting that the photochemical reactions occurred on the external surface. Since the external surface of ZSM-5 seriously restricts the diffusion of the radicals as mentioned above, we propose that the phenol for **4** and the diphenylethane for **3** are produced predominantly on the external surface and are sieved into the internal surface after they are formed.

Photolysis on NaY zeolite—restriction on diffusional and rotational motions

The product distributions for photolyses of **1**–**4** adsorbed on NaY zeolite are significantly different from those formed in solution and on ZSM-5. Photolyses of all four esters on NaY zeolite only produce *ortho* rearrangement products. Molecular models suggest that NaY zeolite possessing an 8 Å pore opening to its 13 Å internal supercage would allow facile entry of esters **1–4** into the zeolite internal surface. We believe that the preference for *o*-hydroxyphenones in the products is a consequence of the restriction experienced by the geminate radical pair. Restriction on diffusional motion of the radical pair produced by photolysis of the esters will encourage recombination of the radical pair. As a result, the escape products, diarylethanes and phenols, are not produced. Since formation of *para* rearrangement products requires greater extent of rotational motion of the radicals than that for *ortho* rearrangement, restriction on rotational motion of the radicals will inhibit production of *para* rearrangement products.

These results contrast strongly with those found for photolysis of dibenzyl ketone and its derivatives on faujasite zeolite. For example, Turro and co-workers reported that[1a,f,h,i] photolysis of dibenzyl ketone, BCOB, on dehydrated NaY resulted in diphenylethane in 85% yield and the remaining mass balance is due to isomers of BCOB, 1-(*p*-tolyl)acetophenone (PMAP) and 1-(*o*-tolyl)acetophenone (OMAP). Among the isomerization products PMAP is the major isomer. In the photolysis of *p*-methylbenzyl benzyl ketone under identical conditions the main products are also the coupling products of the benzyl-like radicals and the cage effect is only 19%. The above observations suggest that the radical pair produced by photolysis of BCOB can readily diffuse apart and rotate to a large extent. We believe the different behaviour in photochemical reactions between dibenzyl ketones and esters **1–4** are attributable to the multiplicities of their reactive states. Homolytic cleavage of a bond from the triplet state of dibenzyl ketone results in the triplet radical pair, and the triplet radical pair has to undergo intersystem crossing before recombination. Thus the primary radical pair has enough time to undergo diffusion and decarbonylation (and eventually couple to yield diarylethanes), and to rotate to a large extent resulting in *para* rearrangement product. In contrast, the photochemistry of esters **1–4** starts from the singlet excited state. With slight rotation the primary radical pair generated by photolysis of the esters may undergo recombination to yield *ortho* rearrangement products.

Experimental

Materials and instruments

Phenyl phenylacetate, *o*-tolyl phenylacetate and *p*-tolyl phenylacetate were synthesized[5] and purified by chromatography on silica. Phenyl *o*-tolylacetate was prepared by esterification of *o*-tolylacetic acid[8] with phenol and purified by chromatography on silica.

Acetonitrile and CH_2Cl_2 were spectroscopic grade and used without further purification. Samples of ZSM-5 and NaY zeolite were purchased from Nankai University and baked at 550 °C for 10 h. The ^1H NMR spectra were recorded at 100 MHz with a Varian FX-100 spectrometer. Mass spectra were run on a VG ZAB GC-MS spectrometer. Gas chromatography was performed on a Shimadzu-7A with a 3% OV-17 column.

Photolysis experiments and product analysis

Photoirradiation of esters **1–4** in acetonitrile solution was carried out in a quartz reactor at ambient temperature and the sample was purged with nitrogen for 15 min before photolysis. A 450 W medium pressure Hanovia Hg lamp was employed as the light source. The zeolites were activated at 550 °C for at least 1 h prior to use. For a typical photolysis experiment, *ca.* 500 mg of activated zeolite was charged with the minimum amount of dry CH_2Cl_2 (with care taken to minimize the time in which the sample was exposed to the atmosphere) and then 5.0 mg of the ester in *ca.* 2 ml of CH_2Cl_2 was added to the sample. The bulk of the solvent was removed by placing the sample in a stream of warm, dry air. The solid was subsequently placed in a quartz photolysis reactor. The dry samples were then degassed at a pressure of 10^{-2} mmHg. The samples were maintained under vacuum and tumbled during photolysis at ambient temperature. After irradiation, the samples were soaked with CH_2Cl_2 overnight. The extracted organic solvent was then concentrated and analysed by gas chromatography and identified on the basis of known retention times of authentic compounds, then confirmed by GC–MS.

Acknowledgements

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