

Photochemistry of 4-Chlorophenol and 4-Chloroanisole Adsorbed on MFI Zeolites: Supramolecular Control of Chemoselectivity and Reactive Intermediate Dynamics

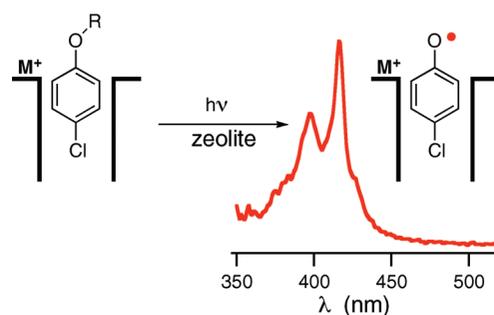
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ABSTRACT



The phototransformation of aryl chlorides adsorbed on MFI zeolites is markedly different from that observed in solution and other solid surfaces such as silica. The formation of radical cations and the constraints imposed by the channels shift the reactivity from the C–Cl bond to the O–R bond. Irradiation generates kinetically stabilized intermediates that can be characterized using conventional steady-state spectroscopic techniques, and these intermediates can be used as ordinary chemical reagents.

MFI zeolites are microporous crystalline aluminosilicates with the general formula $M_x(\text{AlO}_2)_x(\text{SiO}_2)_y$, where M is the charge compensation cation.^{1,2} Their internal surface consists of an

interconnected network of cylindrical channels (diameter ca. 5.5 Å) and intersections (diameter ca. 9 Å). The external surface is composed of a nonporous framework and pore openings. The pore openings on the external surface provide access to the channels and intersections of the internal surface. As a result, only molecules whose size/shape characteristics allow penetration into the holes and whose mobility allows diffusion inside

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the channels will be adsorbed efficiently on the internal surface. This remarkable size/shape selectivity provides zeolites with their selective molecular sieving properties.²

Investigations of the photochemical reactions of molecules adsorbed on MFI zeolites have provided insights to the supramolecular structure and dynamics of intermediates produced by photolysis.^{3–5} The restricted mobility within zeolite pores limits the tendency of radicals, radical cations, or other reactive intermediates to undergo radical-destroying bimolecular reactions and prevents the access to adventitious reagents (e.g., water and oxygen) that would cause their decay in solution. As a result, the trapped reactive intermediates can have lifetimes long enough to be studied by conventional spectroscopic techniques usually reserved for ordinary stable molecules. Carbon centered radicals, for example, can live several hours and be studied spectroscopically on silica and MFI zeolite surfaces.⁶

The phototransformation of aryl chlorides is well established in solution and on silica and cellulose surfaces.^{7–11} The primary photochemical reaction step is the homolytic cleavage of the C–Cl bond to produce a triplet radical pair. In polar environments, electron transfer within the caged radical pair might occur, which leads to an ion pair (phenyl cation + Cl⁻).⁸ The formation of radical cations was also observed in polar solvents.⁸ The main reaction intermediates involved in the phototransformation of aryl chlorides are phenyl radicals (**1**), phenyl cations (**2**), and radical cations (**3**) (Figure 1).^{7–11}

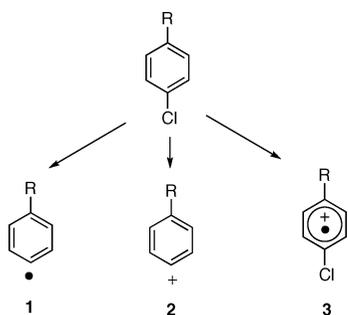
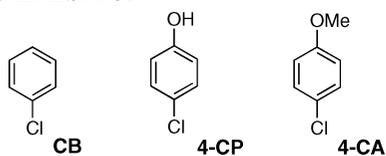


Figure 1. Main photochemical intermediates of aryl chlorides in solution. Intermediate **1** possesses a single electron in a sp^2 orbital localized on the 4-carbon atom. Intermediate **2** possesses an empty sp^2 orbital localized on the 4-carbon atom. Intermediate **3** possesses a half-filled π orbital delocalized over all of the carbon atoms of the benzene ring.

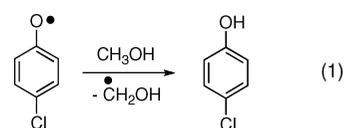
We report here a UV–vis absorption, EPR, and products study of the aryl chlorides chlorobenzene (CB), 4-chlorophenol (4-CP), and 4-chloroanisole (4-CA) on silicalite, Na-ZSM-5, and Li-ZSM-5.



The adsorption of aryl chlorides on MFI zeolites was performed by gas phase adsorption after the zeolite was

initially evacuated to $\sim 10^{-5}$ mmHg (see Figure S1, Supporting Information). Ground state UV–vis diffuse reflectance studies of nonirradiated samples reveal only the guest; no other absorption bands (charge transfer, products) were detected in the spectral region of 250–800 nm. Irradiation leads to the formation of new species that were found to persist for several hours by UV–vis spectroscopy. This long lifetime allowed us to study the reaction intermediates using conventional ground state spectroscopic techniques.

The photochemistry of 4-CP on silicalite was reported previously.⁹ The formation of 4-chlorophenoxy (4-CPO) radicals was observed by diffuse reflectance laser flash photolysis. However, no net reaction of 4-CP was observed by product studies after photolysis, where the samples were extracted with methanol and analyzed by GC-MS. This suggests that 4-CP is regenerated by hydrogen abstraction of 4-CPO radicals from the solvent (methanol) used for extraction (eq 1).



We detected similar UV–vis absorption on all studied zeolites after Hg lamp irradiation (254 nm). The difference diffuse reflectance spectrum, $F(R)_{\text{irradiated}} - F(R)_{\text{nonirradiated}}$, shown in Figure 2, obtained for photolysis of 4-CP on Li-

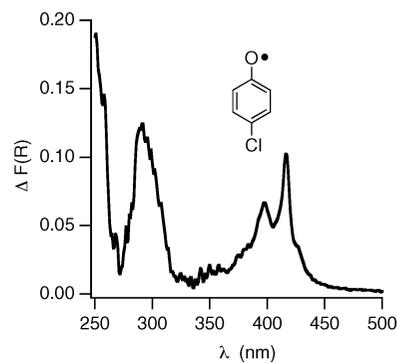


Figure 2. Difference diffuse reflectance spectrum of 4-CP on Li-ZSM5 before and after photolysis at 254 nm. The main peak is assigned to the 4-CPO radical.

ZSM5, shows a vibrational fine structure with maxima at 416 and 397 nm, a feature that is characteristic of 4-CPO radicals.¹² The original diffuse reflectance spectra before subtraction are shown in Figure S2 of the Supporting

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Information. The peak at ~ 290 nm is also assigned to the 4-CPO radical.¹² The minimum of the difference absorption spectrum near 275 nm is probably caused by depletion of ground state absorption of 4-CP.

Little change in the spectra is observed after opening the sample cell to air. In fact, 4-CPO radicals are found to be stable (>12 h) under atmospheric (1 atm of air) oxygen. EPR spectra of photolyzed samples of 4-CP on Li-ZSM5 were recorded. The observed poorly resolved EPR spectrum (Figure 3, black

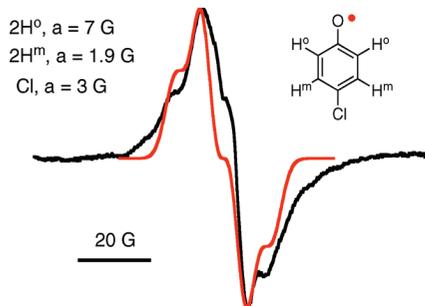
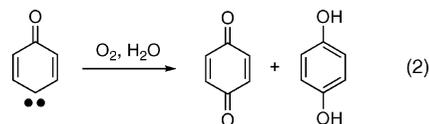


Figure 3. EPR spectrum of 4-CPO radicals (black line) formed by photolysis (254 nm) of 4-CP on Li-ZSM5. Simulated spectrum (red line) using coupling constants shown in inset.

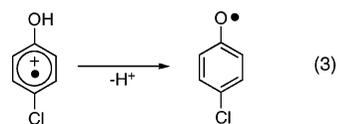
line) is consistent with 4-CPO radicals immobilized on surfaces. The coupling constants between the spin of the odd electron and the proton nuclear spins (a_H) determined by spectral simulation (Figure 3, red line) are in good agreement with literature values for 4-CPO radicals in aqueous solution.^{13,14} The calculated coupling constant between the electron spin and chlorine nuclear spin (a_{Cl}) is slightly higher (3 G) compared to the literature value in solution (1.9 G).^{13,14} Deviations in the coupling constants on zeolite surfaces from published solution values are probably caused by interactions of the adsorbed radical with the polar zeolite surface and metal cations. Significant modifications of the spin density in the phenyl ring by interactions between the radical and metal ions or polar groups of the zeolite surface are known.¹⁵ For details about the EPR analysis and simulation, see the Supporting Information.

Addition of methanol vapor to the irradiated samples quenches the 4-CPO radicals as seen by the disappearance of its absorption at ~ 400 nm (Figure S3, Supporting Information). These radicals abstract hydrogen from methanol and regenerate the starting material 4-CP (eq 1). Therefore, no net reaction is observed by GC-MS analysis of these samples.

We find that the major photo product 4-CPO radical was only observed in significant amounts if the zeolite was dried by calcination at 500 °C for 12 h followed by evacuating to 10^{-5} mmHg for 8 h before loading the sample onto the zeolite (see Supporting Information). Without this temperature and vacuum treatment before probe loading, only small amounts of 4-CPO radicals were observed by UV spectroscopy after photolysis. In the presence of air and water, GC-MS analysis of the methanolic extracts showed the formation of benzoquinone and hydroquinone (Figure S4, Supporting Information), which are the same photo products reported on silica surfaces.¹⁰ In this case, the primary reaction intermediate is a phenyl cation (**2**, Figure 1). This intermediate forms a carbene^{7,10} that can react with molecular oxygen and/or water, leading to benzoquinone and hydroquinone, respectively (eq 2).



The adsorption of 4-CP into the zeolite channels changes the chemoselectivity of reaction compared to that of solution. For example, C–Cl cleavage is observed in the photolysis of 4-CP in aqueous solution⁷ and on surfaces such as silica and cellulose,¹⁰ whereas for 4-CP in zeolite channels O–H cleavage occurs. This observation excludes transients **1** and **2** (Figure 1) as main intermediates since the products would not possess a chlorine atom, leaving radical cations (**3**) as the key plausible chemical intermediates. The formation of radical cations of organic molecules in zeolites is quite common.^{5,16,17} To best of our knowledge, the UV–vis absorption of the 4-CP radical cation is not reported in the literature. However, we expect an absorption at a similar spectral region to cation radicals of 4-CA, which are known to absorb near 475 nm.⁸ In Figure 2, no absorption near 475 nm was observable. The lack of detectable cation radicals for 4-CP is probably due to a fast deprotonation process, a commonly observed reaction for radical cations containing OH groups.¹⁸ Deprotonation leads to 4-CPO radicals (eq 3).



In the case of CB or 4-CA, which do not contain OH groups for deprotonation, radical cations are readily observable near 450 to 475 nm.^{8,19} Photolysis of CB and 4-CA adsorbed on dry zeolites yielded detectable cation radicals (Figure 4 and S5, Supporting Information). For wet zeolites

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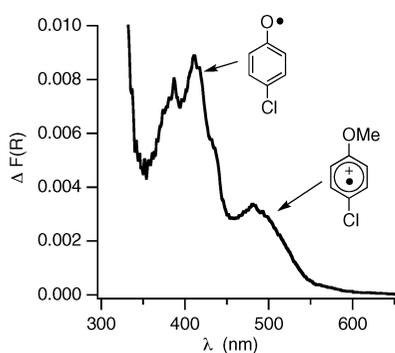
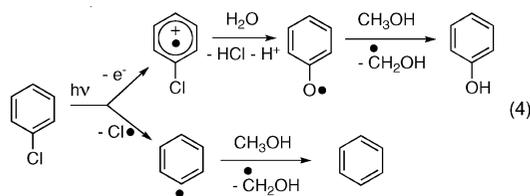


Figure 4. Difference absorption spectrum of 4-CA on silicalite with <0.2% w/w of water before and after photolysis at 254 nm. The assigned chemical structures of the bands as shown.

(<0.2%, w/w) in addition to cation radicals, the absorption bands of phenoxyl radicals and 4-CPO radicals were observed for CB and 4-CA, respectively (Figure 4 and S5, Supporting Information). Photoproduct studies show the formation of phenol and 4-CP, for CB and 4-CA, respectively (eq 4, Figure S6, Supporting Information), thus confirming the assignments (Figures S6–S8, Supporting Information).



Analogous to 4-CP, the adsorption on the zeolite surfaces shifts the photoreactivity of 4-CA from the C–Cl bond to the O–CH₃ bond.

The formation of benzene in the case of photolysis of CB and anisole in the case of 4-CA (eq 4 and Figure S6, Supporting Information) in methanol (minor products, Figures S7 and S8, Supporting Information) suggests the presence of phenyl radicals in the irradiated samples. The final reduction products are formed after hydrogen abstraction from methanol used for extraction (eq 4).

Two plausible orientations for the initial adsorption of the 4-substituted chlorobenzenes are considered: (I) C–Cl bond outside the pore or near an aluminum/exchange cation; (II) C–Cl bond adsorbed into the pore (Figure 5). In both cases, it is assumed that a cation, M⁺, is present near the pore opening. In general, under ambient conditions, water molecules will be available through hydration of the cation.

Supramolecular structure I is considered less plausible based on the following observations. First, interaction between the C–Cl of the aryl chloride and the water/zeolite surface is expected to be weaker for I than with II, the latter allowing for hydrogen bonding. In orientation I, the C–Cl bond experiences a polar environment, and therefore the expected photoreactivity of 4-CP and 4-CA would be that of the phenyl cation (Figure 1, structure 2).^{7–11} When water is present, this intermediate

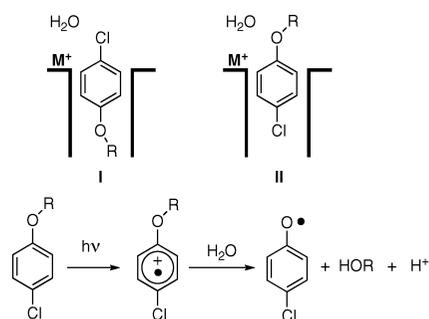


Figure 5. Possible guest orientations in the zeolite channels and main reaction steps.

leads to hydroquinone for 4-CP¹⁰ and 4-hydroxyanisole for 4-CA.¹¹ However, these products were not observed for samples prepared with the addition of water (<0.2%, w/w) (Supporting Information). The photoproduct distributions instead indicate that C–Cl bond is stabilized relative to the O–R bond. In agreement with the main final product, 4-CPO radicals were observed for both compounds, 4-CP and 4-CA. This suggests that supramolecular structure II (Figure 5) is the preferred configuration.

Orientation II easily explains the observed spectra and products. After the formation of the radical cation, deprotonation occurs¹⁸ (eq 3), leading directly to the 4-CPO radical. In the presence of water and for substituents other than H, the radical cation reacts with water (nucleophile) and also forms 4-CPO radicals (Figure 5), probably through an OH-adduct.²⁰

In conclusion, spectroscopic and product analysis data showed that the photo reaction of oxygen-containing aryl chlorides adsorbed on ZSM-5 zeolites depends on the orientation of the guest at the adsorption sites. This orientation, together with the formation of the aryl chloride radical cations and the constraints imposed by the channels, shifts the photoreactivity from the C–Cl bond, well established in solution and on surfaces such as silica, cellulose and cyclodextrin, to the O–R bond. Orientation II (Figure 5) is considered to be the more plausible supramolecular structure involved in the photochemistry.

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Supporting Information Available: Experimental procedures, diffuse reflectance spectra, GC-MS data, details on EPR experiments and simulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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