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# A comparative study of the photophysics and photochemistry of 4-chlorophenol adsorbed on silicalite and $\beta$ -cyclodextrin

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## Abstract

The photochemistry and photophysics of 4-chlorophenol (4-CP) were studied onto two model solid supports, silicalite and  $\beta$ -cyclodextrin ( $\beta$ -CD), using time resolved diffuse reflectance techniques and product degradation analysis. The results have shown that the photochemistry and photophysics of 4-CP are different from solution and depend on the solid. Ground state diffuse reflectance and time resolved luminescence demonstrated the inclusion of the probe in both substrates. 4-CP exhibits room temperature luminescence in both hosts, being structured and much more intense in  $\beta$ -CD. The emission was assigned to phosphorescence of the inclusion complex. Transient absorption demonstrated the formation of the unsubstituted phenoxyl radical and of 4-chlorophenoxyl radical in  $\beta$ -CD. In silicalite only the later was detected. The studies of the photodegradation products indicate that phenol is the main photoproduct in  $\beta$ -CD. In silicalite the chromatographic analysis indicates the presence of products that involve the ring cleavage.

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**Keywords:** Chlorophenol; Silicalite;  $\beta$ -Cyclodextrin; Diffuse reflectance; Laser flash photolysis

## 1. Introduction

The application of flash photolysis techniques to opaque samples was developed by Wilkinson and co-workers in the 1980s [1–4]. It is expected that the laser diffuse reflectance flash photolysis technique will play to heterogeneous systems, a role as important as flash photolysis in the transmission mode for homogeneous media [5]. In spite of this potentiality, works applying this technique to study the photochemistry of pollutants at the solid/gas interface are still very few [6]. This is an important research field since pollutants like pesticides are mainly located at the solid/gas interface [7]. Given the importance of this area and also of our experience with diffuse reflectance and analytical techniques [5,6,8–10], we have started the study the photochemistry of pollutants in model solid systems.

Chlorinated phenols are an important class of environmental pollutants known by their general resistance to chemical and biological degradation in environmental conditions [11]. It is accepted that photochemical transformations in environmental systems play a major role in determining their behaviour and fate. Chlorophenols are widespread in the

environment and its photochemistry is largely documented in solution (see Burrows et al. [12] and references therein).

The photolysis of mono-chlorophenols in aqueous solution was studied in detail by Boule and co-workers [13–15]. For 4-chlorophenol (4-CP), product distribution depends on the dissolved oxygen and also of 4-CP concentration. In air-saturated solutions benzoquinone is the main photolysis product. At low concentrations, it mainly results from direct photo-oxidation of 4-CP while at higher concentrations, its formation results from both molecular and bimolecular reactions. In deoxygenated solutions, at lower concentrations, hydroquinone is the main product while at higher concentrations 5-chloro-2,4'-dihydroxybiphenyl prevails.

The mechanism of solution photoreaction of 4-CP was studied in detail by nanosecond laser flash photolysis [16,17]. Transient absorption spectroscopy gave evidence for the heterolytic character of the process and also revealed the formation of carbene 4-oxocyclohexa-2,5-dienylidene (1), by elimination of HCl from the substrate (see Fig. 1). The other transients formed in acid aqueous solutions and in alkanols (benzoquinone *O*-oxide (2), and unsubstituted phenoxyl radical (3)) and the final transformation products are easily accounted for by the reactions of this carbene. Triplet–triplet absorption was detected in *n*-hexane and 4-chlorophenoxyl radical was formed by photoionization

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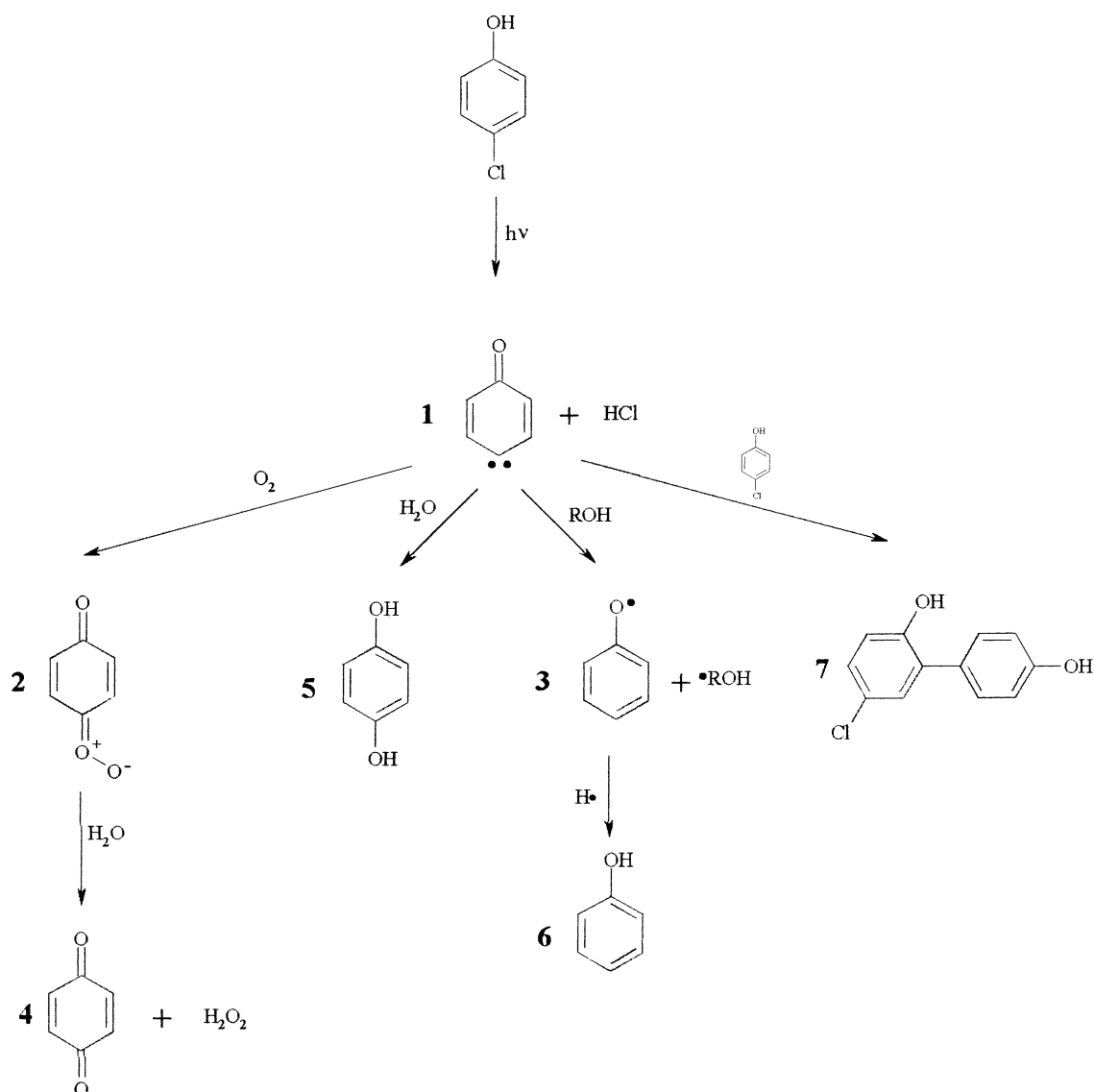


Fig. 1. Mechanism of solution photochemistry of 4-CP.

(two-photon process in neutral aqueous solution and acetonitrile, and one photon process in alkaline aqueous solution).

Photoinduced and photocatalytic degradation of chlorophenols has also been the subject of several investigations [18–23]. The photocatalytic degradation and mineralization by  $\text{TiO}_2$  is one of the most important tools to achieve the destruction of these pollutants [18,22,23]. As a rule, hydroxyl radicals have been implicated as the reactive species in these processes. Oxygen also plays an important role [12–23]. However, other studies have suggested other possibilities. Draper and Fox [18] failed to detect any of the expected intermediate  $\text{OH}^\bullet$  adducts following diffuse reflectance flash photolysis, in the presence of several forms of  $\text{TiO}_2$ . To elucidate the reaction mechanism a diffuse reflectance FTIR investigation was made to study the photocatalytic degradation of 4-CP by  $\text{TiO}_2$  particles in a solid/gas system [23]. The main product of degradation was hydroquinone

and the complete degradation of 4-CP requires the presence of oxygen.

Silicalite is a dealuminated analog of ZSM-5 zeolite. The lack of substitutional aluminium results in silicalite having no significant catalytic or ion exchange properties, compared with other ZSM-5 zeolites. Silicalites are the only known hydrophobic forms of silica and are capable of adsorbing organic molecules up to about 0.6 nm of kinetic diameter [24–27].

Cyclodextrins are cyclic oligosaccharides with 6 ( $\alpha$ ), 7 ( $\beta$ ) or 8 ( $\gamma$ ) D-glucose units, which have a relatively non-polar cavity [26]. They are able to include, in aqueous solution, a variety of compounds whose character may vary from hydrophobic to ionic [26–31]. The inclusion deeply affects the guest properties, being usually associated with a decrease in the rate of non-radiative processes and in the rotational freedom and/or with the elimination

of water molecules surrounding the probe up inclusion [26–31].

In this paper, we report transient absorption and emission studies of 4-CP adsorbed onto two powdered solid supports:  $\beta$ -cyclodextrin ( $\beta$ -CD) and silicalite. The major degradation products were identified and the main degradation paths established.

## 2. Experimental

### 2.1. Materials

4-CP, phenol, hydroquinone, benzoquinone,  $\beta$ -CD (Aldrich), silicalite (Union Carbide), methanol, acetonitrile and *iso*-octane (Merck Lichrosolv) were used without further treatment. Water was deionized and distilled.

### 2.2. Sample preparation

Samples containing 100, 200 and 500  $\mu\text{mol g}^{-1}$  of 4-CP in silicalite were prepared by adding a solution of probe in *iso*-octane (solvent that is not able to penetrate into silicalite channels) to the correspondent quantity of the adsorbent, as described in a previous work with silicalite [27]. Samples were continuously mixed with a magnetic stirrer until all the solvent was evaporated. The removal of the probe from the external surface of the substrate was done using *iso*-octane again (three aliquots, 5 ml each). Finally, the samples were dried under reduced pressure ( $\sim 10^{-3}$  mbar). Solid 4-CP/ $\beta$ -CD complexes of molar ratios 1:1, 1:2.5, 1:5, 1:10 and 1:20 were prepared by mixing a saturated solution of  $\beta$ -CD ( $\sim 10^{-2}$  M) with the correspondent solution of the probe, both in water. The resulting mixture was then magnetic stirred during 48 h and then lyophilised (Heto, Model FD 1–110). By washing the samples with dichloromethane the non-complexed 4-CP was removed. Final traces of the solvent were removed under reduced pressure. Mechanical mixtures were also prepared in silicalite (200 and 400  $\mu\text{mol g}^{-1}$ ) and in  $\beta$ -CD (1:2.5 mol:mol).

The removal of oxygen was achieved by purging argon and the saturation of  $\text{O}_2$  was made using a flow of this gas. Samples were kept under gas flow at least during 1 h.

### 2.3. Methods

#### 2.3.1. Diffuse reflectance ground state absorption spectra

Ground state absorption spectra of the solid powdered samples were recorded using a Cintra 40 GCB Scientific Equipment spectrophotometer, with a diffuse reflectance attachment. The measured reflectance,  $R$ , was used to calculate the remission function  $F(R)$  using the Kubelka-Munk equation defined by

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}$$

where  $K$  and  $S$  are the absorption and scattering coefficients, respectively. The Kubelka-Munk equation applies to optically thick samples, i.e. those where any further increase in the thickness does not affect the experimentally determined reflectance. For an ideal diffuser, where the radiation has the same intensity in all directions,  $K = 2\varepsilon C$ , where  $\varepsilon$  is the Naperian absorption coefficient and  $C$  the concentration. Since, the substrate usually absorbs at the excitation wavelength,  $F(R)_{\text{probe}} = F(R) - F(R)_{\text{substrate}} = \sum_i 2\varepsilon_i C_i / S$ , where  $F(R)_{\text{substrate}}$  is the blank obtained with a cell containing only substrate. Whenever, the probe is only in the form of monomer, this equation predicts a linear relationship for the remission function of the probe as function of the concentration (for a constant scattering coefficient).

#### 2.3.2. Diffuse reflectance laser flash photolysis system and laser induced luminescence

Laser flash photolysis experiments were carried out with the fourth harmonic of a YAG laser (266 nm, 6 ns FWHM, 10–30 mJ per pulse) from B.M. Industries (Thomson-CSF), model Saga 12–10, in the diffuse reflectance mode. A schematic diagram of the system is presented in reference [5]. The light arising from the irradiation of the solid samples by the laser pulse is collected by a collimating beam probe coupled to an optical fiber (fused silica) and detected by a gated intensified charge coupled device (ICCD, Oriel model Instaspec V) after passing via a compact fixed imaging spectrograph (Oriel, model FICS 77440). The system can be used either by capturing all light emitted by the sample or in time resolved mode, using a delay box (Stanford Research Systems, Model 96335). The ICCD has high speed gating electronics (2.2 ns) and intensifier, and works in the 200–900 nm wavelength range. Time resolved absorption and emission spectra are available in the nanosecond to second time range.

Transient absorption data are reported as percentage of absorption (% Absolute) defined as  $100\Delta J_t / J_0 = (1 - J_t / J_0)100$ , where  $J_0$  and  $J_t$ , are the diffuse reflected light before exposure to the laser pulse and at time  $t$  after excitation, respectively. In all samples, the initial transient absorption ( $\leq 20\%$ ) increased proportionally with laser intensity, given evidence for the validity of this treatment, rather than the Kubelka-Munk analysis [28,31].

#### 2.3.3. Irradiation, degradation kinetics and product analysis

Photodegradation studies were conducted in a reactor previously used to study the photochemistry of pesticides [10]. The samples were irradiated at 254 nm using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters and without refrigeration. The photodegradation products were extracted by washing the irradiated samples with methanol. Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph with a 655A-22 UV detector. Analyses were conducted at conversions lower than 10%. UV-VIS spectra of the degradation products

were obtained using the same HPLC system but with a diode array detector (Shimadzu, SPD-M6A). Mass spectra were obtained by GC–MS using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass selective detector (EI 70 eV).

### 3. Results and discussion

#### 3.1. Ground state diffuse reflectance absorption spectra

Ground state absorption spectra of 4-CP (normalised to the maximum absorption) for the two substrates indicate a blue shift when going from  $\beta$ -CD to silicalite (see Fig. 2). The solvatochromic behaviour of  $\pi\pi^*$  bands is well-known: polar and polar protic solvents promote bathochromic shifts because the dipole moment in the excited state is larger than in the ground state [32]. The energy level of the excited state is therefore more stabilised by solvent interaction than ground state. The comparison with solid supports suggests an increase of polarity in the environment of the guest molecule when going from silicalite to  $\beta$ -CD. This explains the deviation of the  $\pi \rightarrow \pi^*$  absorption band to the red with simultaneous loss of the vibrational resolution in  $\beta$ -CD. Silicalite is a well-known structure of interconnecting channels with hydrophobic nature, capable of adsorbing hydrophobic molecules up to about 0.6 nm of kinetic diameter [26]. Fig. 2 results are in accordance with the 4-CP inclusion into silicalite channels.

$\beta$ -CD is considered to have a hydrophobic cavity, but is also hydrophilic outside the cone. This hydrophilic behaviour is related with the presence of the hydroxyl groups in the upper and lower rim of the cone structure. In the formation of host–guest complexes with detergents, the hydrophobic part of the guest is located inside the cavity while the cationic group is placed outside [30]. Interaction with

hydroxyl groups has been implicated in the decarboxylation catalysis of methylphenylcyanoacetic acids by inclusion in  $\beta$ -CD [33]. Therefore, some interaction between 4-CP and the external hydroxyl groups is expected. That is the reason why 4-CP feels a polar environment. The bathochromic behaviour of the absorption band can be interpreted by considering inclusion and strong specific interaction of the probe with the hydroxyl groups of the substrate external surface.

Mechanical mixtures in both substrates present the same intensity and spectral distribution as samples with the same concentrations but prepared using the solvent. This suggests that inclusion occurs even without the aid of the solvent. The vapour pressure of 4-CP crystals is around 1 mmHg at 50 °C [34], suggesting that inclusion could occur from the gas phase. This has been observed for silicalite [35]. Little difference in ground state absorption spectra of washed and unwashed samples was found (within the experimental error). This result confirms once more the inclusion in both substrates.

#### 3.2. Laser induced luminescence

Time resolved emission spectra of 4-CP in  $\beta$ -CD is shown in Fig. 3. For comparison purposes Fig. 4 presents the emission spectra of an ethanolic solution at 77 K. Based also on the spectral localisation and on the decay kinetics the band observed at low temperature and centred at 390 nm, was attributed to emission from the triplet state. The emission from  $\beta$ -CD is similar to the observed at 77 K and was assigned to phosphorescence of 4-CP included in the cavity. Room temperature phosphorescence induced by inclusion in  $\beta$ -CD has been studied for aromatic compounds [27–31]. This phenomenon is usually associated with a decrease in the rate of non-radiative processes and in the rotational freedom and/or with the elimination of water molecules surrounding the fluorescence probe included in the cyclodextrin cavity. It can

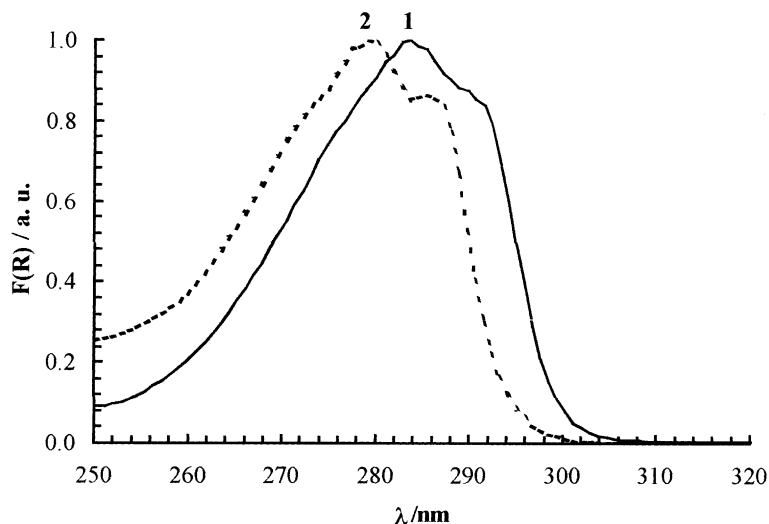


Fig. 2. Remission function, normalised to the absorption maximum, of 4-CP adsorbed on  $\beta$ -CD (1) and on silicalite (2).

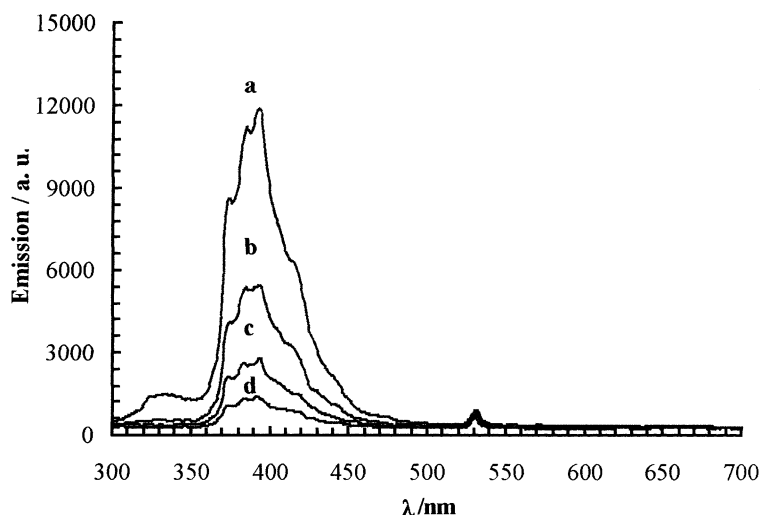


Fig. 3. Laser induced room temperature phosphorescence spectra of 4-CP, following 266 nm excitation ( $\sim 20$  mJ per pulse), in cyclodextrin: 250 ns (a), 500 ns (b), 750 ns (c), and 1000 ns (d), after the laser pulse.

therefore be concluded that 4-CP is included into the  $\beta$ -CD cavity, which is in agreement with the ground state absorption spectra results.

Silicalite can also induce room temperature phosphorescence [25–28]. This has been attributed to restrictions in the molecular motion [25]. However, included valerophenone shows some mobility, which allows photochemical reaction and suppresses the luminescence. The emission of 4-CP in silicalite is non-structured and much less intense than in  $\beta$ -CD, suggesting the existence of non-radiative channels that efficiently compete with triplet formation or deactivate this state. The smaller phosphorescence emission in silicalite can therefore be attributed to the existence of a photodegradation pathway present in this host, as we will show later with transient absorption results.

Small oxygen effect was observed for samples in silicalite and  $\beta$ -CD. This result has also been reported for some aromatic ketones [28,30,31] and was attributed to the probe inclusion, which restricts the oxygen mobility and the possibility of quenching in both substrates. The slight oxygen effect on the luminescence can therefore be attributed to restrictions on its mobility towards included 4-CP.

### 3.3. Diffuse-flectance laser flash photolysis and degradation products

Time resolved absorption spectra and decay kinetics of 4-CP in silicalite and  $\beta$ -CD were obtained by the use of the set-up described above, which allowed us to obtain time resolved absorption spectra with nm-spectral resolution.

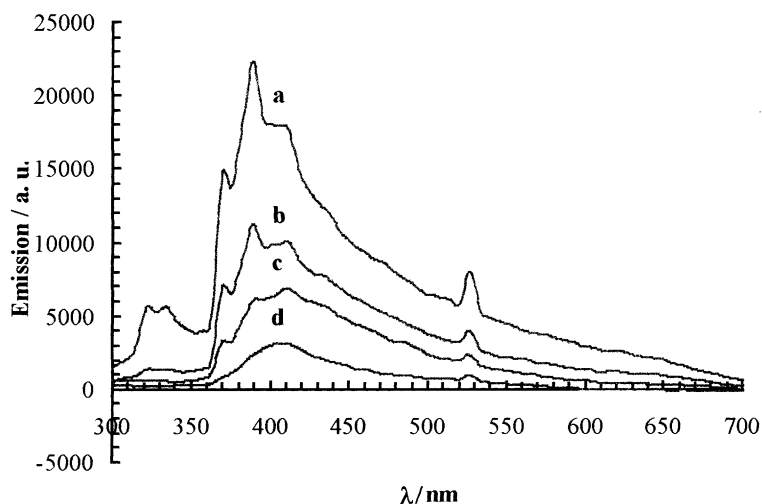


Fig. 4. Laser induced luminescence spectra of 4-CP, following 266 nm excitation ( $\sim 20$  mJ per pulse), in ethanol glass (at 77 K): 250 ns (a), 500 ns (b), 750 ns (c), and 1000 ns (d), after the laser pulse.



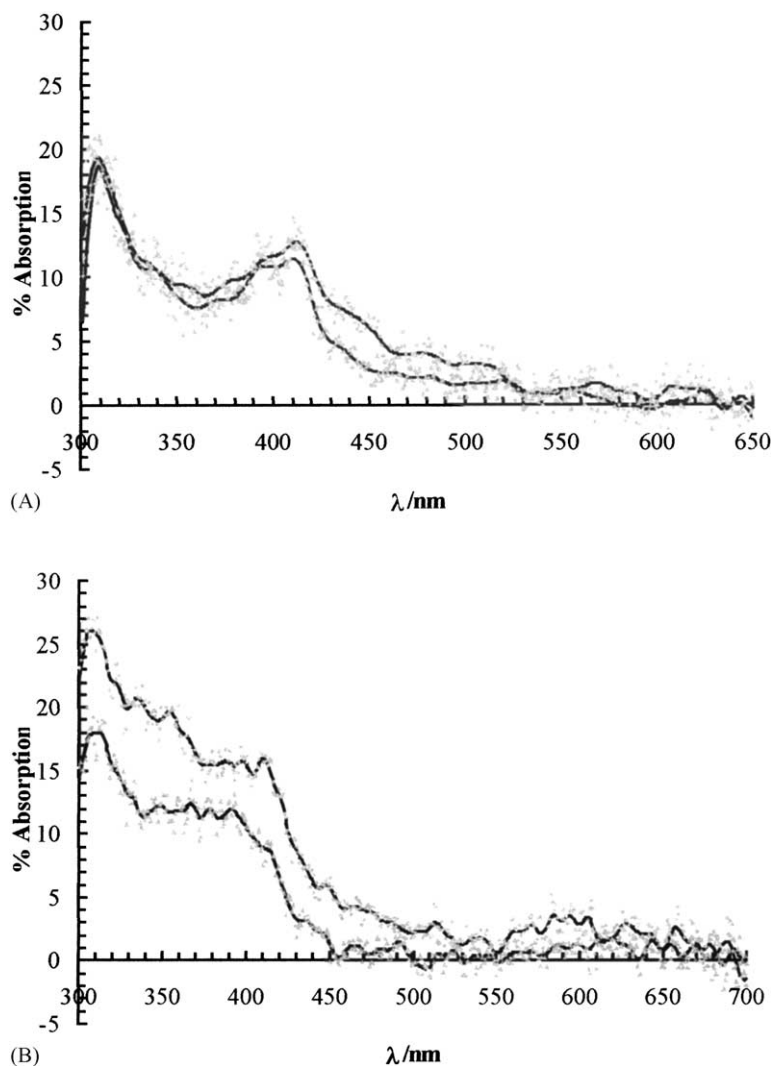


Fig. 5. Transient absorption for 4-chlorophenol, upon irradiation at 266 nm ( $\sim 20$  mJ per pulse), adsorbed on silicalite (A), and on  $\beta$ -cyclodextrin (B), at pulse end (upper spectrum) and 20 ms after the laser pulse (lower spectrum).

Fig. 5 shows the transient absorption spectra of 4-CP in both substrates at pulse end and after 20 ms. The results indicate that the photochemistry depends strongly on the substrate. In silicalite a very well resolved main absorption is detected, with maxima at 413 and 400 nm. This band is similar in its spectral localisation and vibrational spacing to the well-known absorption of the 4-chlorophenoxy radical in solution [16,17,21,22]. This band was therefore assigned to this radical and to our knowledge, this is the first time that this radical is reported in solid samples. The band centred at 310 nm can also be attributed to the 4-chlorophenoxy radical [22].

In  $\beta$ -CD the 4-chlorophenoxy absorption band is also present, although less resolved. A much less intense band can also be seen around 600 nm. The unsubstituted phenoxy radical has a medium intensity absorption band with maxima at 380 and 400 nm [17,36] and a low intensity band around 600 nm [36]. This small absorption band which appears in

$\beta$ -CD is due to a low intensity  $\pi\pi^*$  absorption band [36] of the unsubstituted phenoxy radical. In fact, after 20 ms, this band is still present and the maxima of the medium intensity band are blue shifted (380 nm and 400 nm). This result indicates that the medium absorption band present at pulse end is due to the double absorption of the unsubstituted phenoxy radical and of the 4-chlorophenoxy radical, being the former much more persistent.

Similar absorption spectra were obtained upon argon-degassing and oxygen saturation, in both substrates. This result is in agreement with the slight oxygen effect observed on the luminescence emission processes. We were not able to detect any absorption band that we could simply assign to triplet-triplet absorption, similar to the one published in hexane by Grabner et al. [17].

The unsubstituted phenoxy radical is readily detected by flash photolysis of 4-CP in argon-purged alkanol solutions. Its formation in these solvents was interpreted

considering the formation of the carbene 4-oxocyclohexa-2,5-dienylidene followed by hydrogen abstraction (see Fig. 1). Although not detected in these solvents, the involvement of this carbene in the production of the unsubstituted phenoxyl was suggested by the formation of benzoquinone *O*-oxide in the presence of oxygen, a transient produced by the carbene (see Fig. 1) [17]. The unsubstituted phenoxyl formation in  $\beta$ -CD is thus plausible since this host supplies to 4-CP an environment similar to that in alkanols. However, there is no evidence of the carbene formation since it was not detected nor even the benzoquinone *O*-oxide in oxygen saturated atmosphere.

Flash photolysis showed that the 4-chlorophenoxyl radical is formed from 4-CP by a photoionization two-photon process in neutral aqueous solution and acetonitrile, and one photon process in alkaline aqueous solution [17]. One important path for unsubstituted phenoxyl radicals is the electron photoejection followed by deprotonation of the radical cation [37]. The 4-chlorophenoxyl radical was produced by oxidation of 4-CP followed by deprotonation of the corresponding radical cation [21]. Therefore, a way to produce this radical on solid samples could be initiated by electron photoejection. One of the most important mechanisms of photoejection is two-photon absorption [37,38]. This mechanism is usually operative when the transient absorption as function of the pulse energy shows a quadratic dependence. We made a careful study of the 4-chlorophenoxyl absorption as function of the laser pulse energy (between 5 and 30 mJ per pulse). That study shows a linear dependence, and this result does not support the biphotonic processes [38]. One possible way to produce the 4-chlorophenoxyl radical in our solid samples could be initiated by electron photoejection followed by deprotonation of the radical cation.

The detected photodegradation products are different in silicalite and in  $\beta$ -CD, which reflects the differences observed in the transient absorption results. In  $\beta$ -CD phenol is the main degradation product, as detected by HPLC. The

identification was based on the analysis of an authentic sample. This compound should be formed by hydrogen abstraction of the unsubstituted phenoxyl radical. Since, no spectral evidence was found for the carbene, the unsubstituted phenoxyl radical formation must follow a different path, as suggested for the formation of phenol by photodegradation of 4-CP in hexane [17]. For samples with conversions lower than 10%, none of the usual degradation products in water was detected.

The photodegradation in silicalite is reduced when compared with  $\beta$ -CD. This confirms that a different degradation path is operative. Phenol is only formed in high concentrated samples (500  $\mu\text{mol g}^{-1}$ ). For low concentrated samples none of the products usually formed in solution was detected. The spectra of the detected photoproducts, extracted with methanol and obtained with the used photodiode array detector, showed no evidence of the  $\pi \rightarrow \pi^*$  transition band, characteristic of benzene derivatives. In fact only a band centred at 230 nm was observed, and this is an evidence for the breakdown of the ring. GC-MS spectra have confirmed this result. One of the spectra showed a molecular ion at  $m/z = 116$  and the presence of chlorine. The comparison with the spectra of the library HP nbs54 k.1 suggested the compound 3-chloro-2-cyclopenten-1-one, with a quality of 95%.

The main degradation pathway of 4-CP in  $\beta$ -CD involves the formation of the unsubstituted phenoxyl radical, which yields phenol as the main degradation product (see Fig. 6). In silicalite 4-chlorophenoxyl is the main transient, and the main degradation products involve the breakdown of the ring.

The photophysics and photochemistry of 4-CP in solids supports is markedly different from solution. This was already found for pesticides [9] and suggests that photochemical studies of pollutants should be made in conditions as similar as possible to those observed in natural systems. The photoproduct distribution indicates major dechlorination of 4-CP in  $\beta$ -CD, with consequent formation

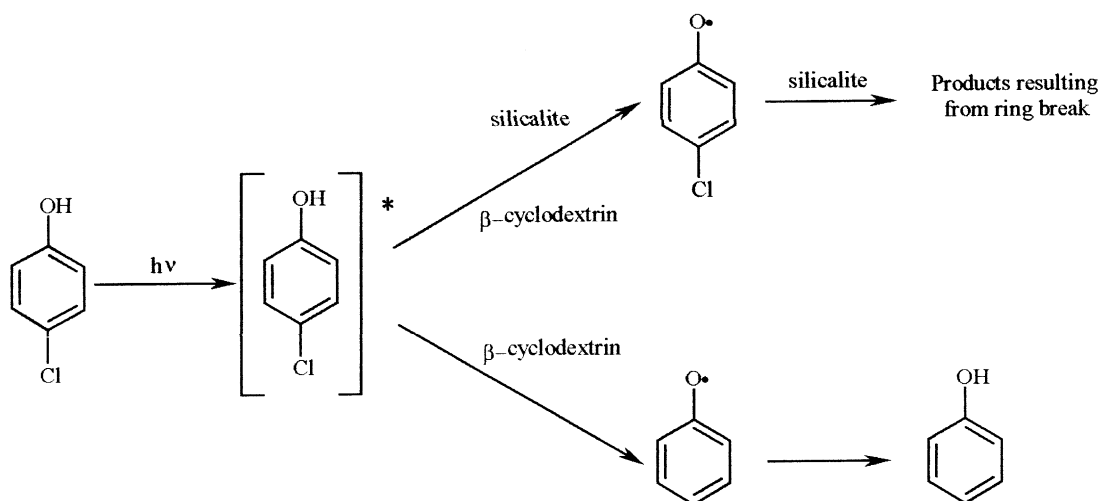


Fig. 6. Scheme of the degradation paths of 4-CP on silicalite and  $\beta$ -CD.



of non-chlorinated products, which are friendlier from the environmental point of view. This suggests that the photodegradation at solid/gas surfaces could be used to transform pollutants in less toxic and less persistent products.

#### 4. Conclusions

Photochemistry and photophysics of 4-CP in solid surfaces are markedly different from solution and depend on the solid substrate. Its inclusion in  $\beta$ -CD originates room temperature phosphorescence emission. In silicalite a less intense and unstructured emission was observed. Transient absorption showed the formation of the unsubstituted phenoxyl radical and of the 4-chlorophenoxyl radical in  $\beta$ -CD. In silicate only the later was observed. Photodegradation studies indicate the formation of phenol in  $\beta$ -CD and ring cleavage in silicalite. Studies of pollutants should be made in conditions as similar as possible to those observed in natural systems. Photodegradation at solid/gas interfaces can be an alternative way to eliminate residues of pollutants and treat contaminated systems.

#### Acknowledgements

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