The Photochemistry of 4-Chlorophenol in Water Revisited: The Effect of Cyclodextrins on Cation and Carbene Reactions

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Abstract: The photochemistry of 4-chlorophenol (**1**) in water and in the presence of cyclodextrins has been studied by means of steady-state and time-resolved experiments. These have shown that **1** undergoes photoheterolysis of the C–Cl bond in the triplet state to yield the 4-hydroxyphenyl cation ^{3}**2** in equilibrium with 4-oxocyclohexa-2,5-dienylidene, ^{3}**3**. These triplet intermediates scarcely react with a n nucleophile, such as water, nor abstract hydrogen from this solvent, thus they are long-lived (≈ 1 μs). Specific trapping of both intermediates has been achieved. The cation adds to 2-propenol, $k_{add} \sim 1.3 \times$ $10^8 \, \text{M}^{-1} \, \text{s}^{-1}$, to form the long-lived phenonium ion **11** (with $\lambda_{max} = 290$ nm), which then converts to 3-(4-hydroxyphenyl)propane-1,2-diol (**10**). Carbene ^{3}**3** is trapped by oxygen to give benzoquinone and is reduced by D-glucose ($k_q = 8.5 \times 10^6 \, \text{M}^{-1} \, \text{s}^{-1}$) to give the phenoxyl radical (**8**) and phenol (**9**). Cyclodextrins have been found to trap the intermediates much more efficiently ($k_q = 9.4 \times 10^8 \, \text{M}^{-1} \, \text{s}^{-1}$ with β-CD),

which indicates that inclusion is involved. Ground state **1** forms inclusion complexes with 1:1 stoichiometry and association constants of 140 and $300 \, \text{M}^{-1}$ with α- and β-CD, respectively. Complexation does not change the efficiency or the mode of photofragmentation of **1**; however, it does influence the course of the reaction because the major portion of the intermediates are reduced to phenol within the cavity ($k'_{red} \geq 5 \times 10^7 \, \text{s}^{-1}$) either via a radical **8** or via a radical cation **9$^+$**. Under these conditions, neither 2-propenol nor oxygen trap the intermediates to a significant extent.

Introduction

Photoinduced dehalogenation of aryl halides has received much attention in recent years because it is both a clean procedure for the destruction of widespread pollutants[1–3] and a tool for the production of intermediates useful for synthetic applications.[4] The photodegradation mechanism of monochlorophenols has been investigated by steady-state and time-resolved techniques and product studies. The conclusions obtained for 4-chlorophenol (**1**) in water are outlined in Scheme 1. Triplet 4-oxocyclohexa-2,5-dienylidene **3**, referred to as "carbene" in the following, carefully characterized by Grabner's and other groups,[5–7] is thought to be a
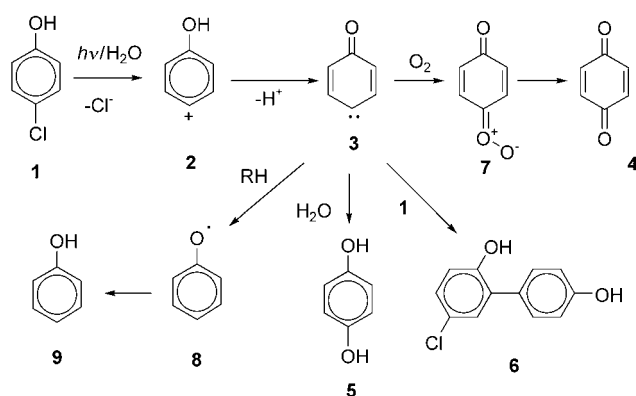
Scheme 1. Photochemistry of **1** in water as reported in reference [5].

key intermediate. This may arise either from a concerted HCl elimination or from a two-step process involving heterolytic cleavage of the C–Cl bond in triplet **1** to yield the hydroxyphenyl cation **2** and deprotonation; however, the latter intermediate has not been detected.[5,7] In water, the main photoproducts are *p*-benzoquinone (**4**), hydroquinone (**5**),

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and 5-chloro-2,4′-dihydroxybiphenyl (**6**). They have been rationalized as resulting from the reaction of carbene **3** with oxygen (via benzoquinone-*O*-oxide **7**), water, and **1**, respectively. In the presence of a H donor, such as an alcohol, carbene **3** transforms through a different transient, the phenoxyl radical **8**, which is further reduced to phenol **9**.[5,7]

Irradiation of **1** in organic solvents in the presence of alkenes or benzene leads to the formation of alkylphenols or hydroxybiphenyls, respectively (Scheme 2).[8] These reac-
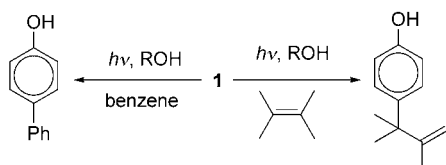
Scheme 2. Photochemical reaction of **1** with benzene and an alkene in organic solvents.[8]

tions have been rationalized as involving cation **2** in the triplet state, on the basis of the analogy with the corresponding reactions of 4-chloroaniline, for which formation of the corresponding cation and its selective reaction with π nucleophiles, not *n* nucleophiles, have been demonstrated.[9]

Moreover, a detailed mechanistic study of the photochemistry in alcohols of 2,6-dimethyl-4-chlorophenol, chosen to minimize the formation of biphenyl derivatives such as **6**,[10] has demonstrated that the corresponding cation **2′** and carbene **3′** are formed *in equilibrium* and each one gives its own typical reactions, that is, trapping by an alkene or by
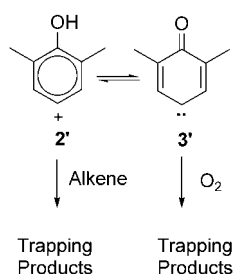
Scheme 3. Intermediates in the photochemistry of 2,6-dimethyl-4-chlorophenol.[10]

oxygen, respectively (see Scheme 3). Although the cation was not directly detected, secondary transients arising from both intermediates were observed by time-resolved spectroscopy and were assigned so that a complete kinetic characterization of the system was achieved.

In view of this novel evidence it appeared appropriate to revisit the photochemistry of the parent 4-chlorophenol (**1**) in water in the presence of an alkene to recognize the possible role played by both the 4-hydroxyphenyl cation **2** and carbene **3**. A tool to obtain further insight into the mechanism of this photoreaction was thought to be the use of cyclodextrin (CD) cavities as photoreaction media (Scheme 4).
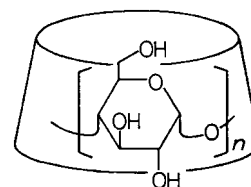
Scheme 4. Schematic representation of cyclodextrins ($n = 6$ for α-CD; $n = 7$ for β-CD).

It was deemed likely that this environment could modify the photochemistry of **1** because a different fate of highly reactive intermediates, such as charged **2** and uncharged **3**, is expected. Previously, Da Silva et al. had investigated the photochemistry of **1** complexed with a solid cyclodextrin by means of time-resolved diffuse reflectance and product studies. Irradiation of a powdered 4-chlorophenol/β-cyclodextrin complex led to the formation of phenol as the predominant photoproduct. The unsubstituted phenoxyl radical was shown to be the main transient in the solid samples.[11]

Cyclodextrins as reaction vessels may provide a suitable environment for enhancing the selectivity and efficiency of bimolecular processes,[12] in this case, of arylation reactions. Herein, we report the photochemistry of **1** in neat water as well as with α-CD and β-CD, including the determination of the association constants, product identification, and time-resolved absorption measurements for recognizing the intermediates and their kinetic evolution.

Results

Inclusion of 4-chlorophenol in CDs: The inclusion of 4-chlorophenol (**1**) in α- and β-CD was studied by measuring the induced circular dichroism (icd). In the case of α-CD, positive icd signals were evidenced in correspondence with the UV absorption bands peaking at 230 nm and at 282 nm. In the case of β-CD, the 230 nm icd band was still positive whereas the icd signal in the low-energy absorption band was negative. A best fit of $|\theta_{max}|$ versus the CD concentration (α-CD in the $0–4\times10^{-2}$ M range, β-CD in the $0–1.4\times10^{-2}$ M range) with a nonlinear equation[13] provided evidence for a 1:1 complexation with equilibrium constants of $140\,\mathrm{M}^{-1}$ and $300\,\mathrm{M}^{-1}$ at 22 °C with α- and β-CD, respectively. The values of the association constants with both α- and β-CD are in good agreement with the values obtained by calorimetric methods.[14]

Photoproducts in the presence of various additives: Irradiation of air-equilibrated aqueous solutions of **1** at 22 °C induced the spectral changes shown in Figure 1a. Bleaching of the 280 nm absorption band of the starting compound was accompanied by growth of the conspicuous band ($\lambda_{max} = 245$ nm) corresponding to *p*-benzoquinone **4**. Parallel experiments with HPLC monitoring indicated **4** as the predominant photolysis product in aerated solutions, while a mixture of products, including a small amount of phenol **9**, resulted
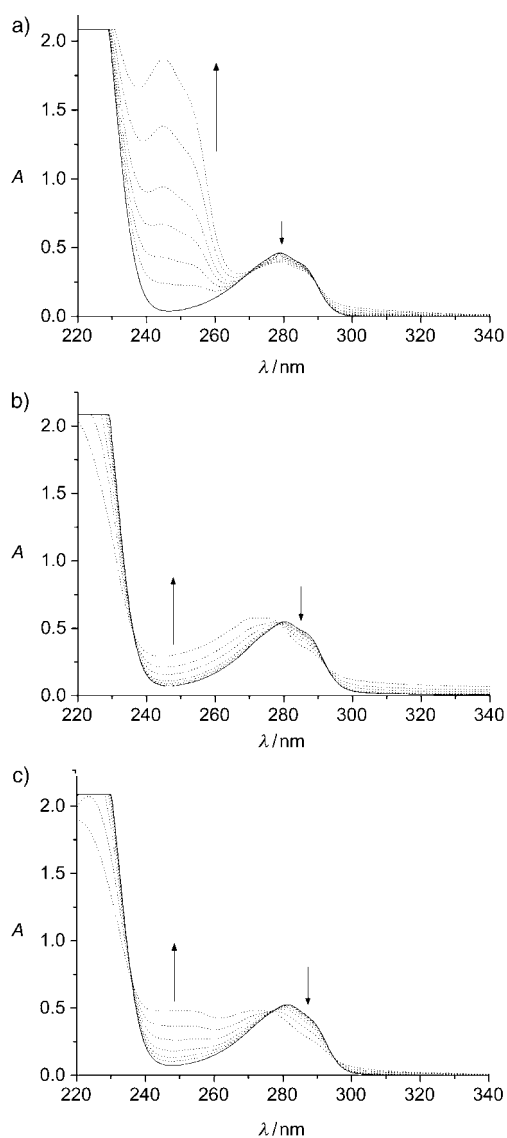
a)

b)

c)

Figure 1. Absorption spectra of air-equilibrated aqueous solution of **1** (0.31 mM). a) Upon irradiation at 282 nm for 0, 3, 6, 10, 15, 25, and 40 min. b) The same, in the presence of α-CD (83% complex) upon irradiation at 282 nm for 0, 3, 6, 10, 25, 45, and 100 min. c) The same, in the presence of β-CD (74% complex) upon irradiation at 282 nm for 0, 3, 6, 12, 25, 50, and 100 min.

Table 1. Dehalogenation quantum yields and product yields for the photolysis of 4-chlorophenol in water in the presence of various additives.[a]

Photolysis conditions		Φ_r	Product (Yield [%])	2-Propenol (0.06 M)	
				Φ_r	Product (Yield [%])
Neat	N$_2$	0.83[b]	**9** (13)[c]	0.71	**9** (10), **10** (80)
	air	0.62	**4** (95)[c]	0.71	**9** (9), **4** (tr), **10** (76)
α-CD, 0.03 M	N$_2$	0.77	**9** (93)	0.95	**9** (53), **10** (9)
	air	0.82	**9** (91), **4** ($\leq$3)		
β-CD, 0.013 M	N$_2$	0.91	**9** (56)	0.92	**9** (36), **10** (27)
	air	0.92	**9** (50), **4** (30)		
D-Glucose, 0.1 M	N$_2$	0.76	**9** (58)	0.65	**9** (12), **10** (73)
	air	0.65	**9** (51), **4** (48)	0.53	**9** (13), **4** (tr), **10** (66)

[a] Irradiation at 282 nm of 1.5×10^{-3} M solutions, unless otherwise noted, up to 10–15% conversion, see the Experimental Section; error ± 0.03. [b] Reference [5]. [c] By the use of a 7×10^{-4} M solution of **1** because a higher concentration resulted in a considerably lower quantum yield owing to the inner filter effect of the photoproducts (this is the cause of reported lower values, $\Phi = 0.44$ in reference [7]).

Scheme 5. Photochemistry of **1** in the presence of 2-propenol.

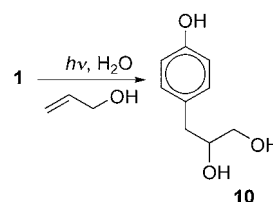from irradiation of a nitrogen-flushed aqueous solution (Table 1), as previously reported.[5,15]

Because experiments in organic solvents had demonstrated that alkenes are a suitable trap for phenyl cations, we explored the photochemisty of **1** in the presence of 2-propenol (0.06 M), a water-soluble alkene. The main photoproduct by far was an arylated glycol, identified as 3-(4-hydroxyphenyl)propane-1,2-diol (**10**). This was accompanied by a small amount of **9** (see Table 1 and Scheme 5). The product distribution showed little change in aerated versus deaerated solutions.

The addition of cyclodextrins significantly influenced the course of the reaction. This is apparent from the UV spectra recorded during the irradiation of **1** in air-equilibrated water (compare Figure 1b and 1c with Figure 1a). With α-CD (83% of **1** complexed) or β-CD (74% of **1** complexed), the p-benzoquinone absorption at 245 nm was reduced or eliminated and the long wavelength band at $\approx$275 nm was shifted to the blue. HPLC monitoring showed that the phenol **9** was by far the main product with α-CD, both in nitrogen- and in air-equilibrated solutions (Table 1), and likewise with β-CD, though some quinone **4** was formed in the presence of air. D-Glucose, as a noncomplexing hydrogen donor, was tested next. This gave mainly phenol **9** in a nitrogen-flushed solution, but equivalent amounts of **9** and **4** in the presence of air.

Finally, the study was extended to the photoreactions in the presence of both CD and 2-propenol. α-CD reduced the yield of adduct **10** to $1/10$ of that in neat water, while the proportion of phenol **9** significantly increased. β-CD induced a similar, although less pronounced effect, whereas in the experiment with glucose, only minor changes of the yields of products **9** and **10** occurred both in nitrogen- and air-equilibrated solutions.

Time-resolved studies: The transients formed by nanosecond laser flash photolysis of **1** in water have been described by Grabner.[5] The earliest detectable species had $\lambda_{max} = 370$ and *384* nm (here and in the following the most intense band is written in italics) and corresponds to carbene **3**

evolving to an unstructured spectrum with $\lambda_{max} = 400$ nm and a time constant on the microsecond scale. Intermediate **3** gave *p*-benzoquinone-*O*-oxide (**7**) ($\lambda_{max} = 460$ nm) by reaction with oxygen (rate constant $3.5 \times 10^9 \, M^{-1} s^{-1}$) and phenoxyl radical **8** ($\lambda_{max} = 385$, *400* nm) by reaction with alcohols in deaerated solutions (rate constants 10^6–$10^7 \, M^{-1} s^{-1}$).[5]

We extended the time-resolved studies to the conditions previously considered for steady-state photolysis. In deaerated solutions, an efficient quenching of the initial intermediate by 2-propenol, α-CD, and β-CD was observed. The rate constants k_q of the bimolecular reaction involving the initial intermediate and the additives were determined, by analyzing the kinetics of the buildup of the absorption at 400 nm, as the slope of the linear plots of k_{obs} versus 4–5 additive concentrations (Table 2, $k_0 = 1.0 \times 10^6 \, s^{-1}$ in neat water

Table 2. Rate constants of the bimolecular quenching of the initially formed intermediate by various additives.

$k_q [M^{-1} s^{-1}]$	H donor
α-CD[a]	$(5.7 \pm 1.0) \times 10^8$
β-CD[a]	$(9.4 \pm 0.2) \times 10^8$
D-glucose	$(8.5 \pm 0.4) \times 10^6$
2-propenol	$(1.3 \pm 0.1) \times 10^8$

[a] A portion of the ground state **1** was complexed by the cyclodextrins in these experiments. This varied from 15% to 62%, depending on the CD concentrations and on the K_{ass} value. The contribution of the ground-state complex to the transient absorption at 400 nm is indicated by the "instantaneous" part of the absorbance change upon laser excitation, which increased with the CD concentration. The k_{obs} values were extracted from the kinetics of the further buildup of the 400 nm absorbance on a longer timescale.

under our experimental conditions). The rate constant measured for 2-propenol, $k_q = 1.3 \times 10^8 \, M^{-1} s^{-1}$ was one order of magnitude higher than that reported for the most reactive alkanols.[5] Furthermore, the evolution of the transient spectra was different (Figure 2). The difference spectrum at 38 ns[16] delay exhibited the features of the carbene absorption in water[5] and then decayed, with pseudofirst-order kinetics, giving rise concomitantly to an intense peak at 290 nm.

Laser flash photolysis experiments were performed on solutions containing about 80% of **1** complexed in the ground state with α- and β-CD. Argon-saturated aqueous solutions excited at 266 nm exhibited the difference absorption spectra reported in Figure 3. An absorption with peaks

Figure 3. Difference absorption spectra of argon-flushed water solution of **1** (1.4 mM) with β-CD (0.015 M, 80% complex) at (■) 0 ns, (○) 20 ns, (△) 40 ns, and (▼) 140 ns after the end of the pulse (2.2 mJ per pulse). The inset shows the 370–410 nm range in detail.

at *385*/400 nm and a shoulder at 420–430 nm formed with a rate constant $k_{fast} \geq 5 \times 10^7 \, s^{-1}$. In the subsequent few tens of nanoseconds ΔA slightly decreased at 250 and 385 nm and increased at 400 nm. The rate constant of this "slow" evolution was $k_{slow} \sim 2 \times 10^7 \, s^{-1}$. At 140 ns, the spectrum exhibiting $\lambda_{max} = 385$/*400* nm resembles that of the phenoxyl radical **8** in water.[17] In the presence of α-CD, the earliest species detected exhibited differential absorption characterized by $\lambda_{max} = 245$ and *385*/400 nm and a shoulder at 420–430 nm. The absorbance changes at 400 nm were about one half those observed with β-CD under comparable conditions (data not shown) In a few hundreds of nanoseconds, ΔA slightly decreased ($k_{slow} \sim 8 \times 10^6 \, s^{-1}$).

Experiments were also carried out with lower concentrations of α- and β-CD. Figure 4 shows the time evolution of the spectra for the case of 25% of the 4-chlorophenol mole-
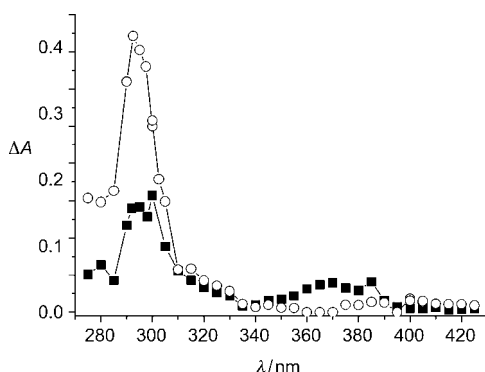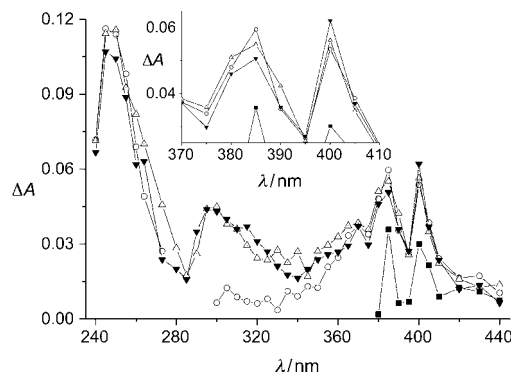

Figure 2. Difference absorption spectra of argon-flushed water solution of **1** (1.4 mM) in the presence of 2-propenol (0.06 M, ■) 38 ns, (○) 0.8 μs after the end of the pulse (2.0 mJ per pulse).
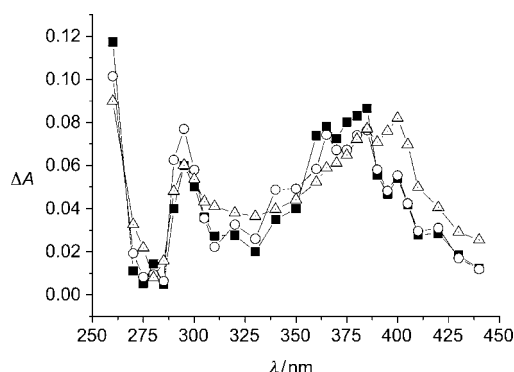

Figure 4. Difference absorption spectra of argon-flushed water solution of **1** (2 mM) with β-CD (1.7 mM, 25% complex) at (■) 140, (○) 200, and (△) 1200 ns after the end of the pulse (2.8 mJ per pulse).

cules associated with β-CD in the ground state. The initial absorption at $\lambda = 370/384$ nm is transformed into a longer wavelength absorption at $385/400$ nm in ≈ 1 μs.

In a subsequent series of experiments, the competition of different additives was studied. In air-equilibrated solutions containing 78% of **1** complexed by β-CD, the 460 nm band of **7** (Figure 5a, trace 1) was almost totally suppressed and the $385/400$ nm transient dominated (Figure 5a, trace 2). The same result was obtained in the case of 80% association of **1** by α-CD. At 60% complexation with β-CD (Figure 6), a small amount of the intermediate **7** was formed over a relatively long timescale ($k_{obs} = 5 \times 10^6$ s^{-1}), while the short-wavelength part of the spectrum with $\lambda_{max} = 365/385/400$ nm decreased with the same kinetics, converting into a spectrum with $\lambda_{max} = 400$ nm. Note that above 500 nm, the transient absorption decreased, whereas the band at 460 nm was still growing. This indicated the presence of a further transient absorbing in the visible, in addition to **7**. With a sevenfold higher concentration of D-glucose rather than β-CD, both of the above transients were significantly present after 0.7 μs (Figure 5b). Again the two bands formed with the same rate constant (Figure 5c, $k_{obs} = 2.2 \times 10^6$ s^{-1}), depending on the D-glucose concentration and decayed with different kinetics. Clearly, CDs have a much higher quenching ability towards the carbene than D-glucose (see Table 2) and compete better with oxygen.

The formation quantum yields of the various intermediates were estimated by means of a comparative method based on the absorption of the hydrated electrons produced by the photolysis of [K$_4$Fe(CN)$_6$] in H$_2$O (quantum yield = 0.52).[18] The assumed molar absorption coefficients were 3000 M^{-1}cm^{-1} at 400 nm for the phenoxyl radical[5,16] and 9500 M^{-1}cm^{-1} at 460 nm for *p*-benzoquinone-*O*-oxide.[5] As shown in Table 3, in the system containing D-glucose, the

Table 3. Formation quantum yields of the intermediates **7** and **8** upon laser flash photolysis of **1** in air-equilibrated water.[a]

Additive	Φ_8	Φ_7
D-glucose (0.1 M)	0.48	0.27
β-CD (1.3×10^{-2} M), 78% complex	0.49	≈ 0.04
α-CD (3×10^{-2} M), 80% complex	0.24	≈ 0.027

[a] Error ± 15%.

Figure 5. a) Trace 1: Difference absorption spectra of air-equilibrated water solution of **1** (0.9 mM) at 3 μs after the end of the pulse (1.4 mJ per pulse). Trace 2: the same, in the presence of β-CD (0.013 M) at 0.7 μs after the end of the pulse (1.4 mJ per pulse). b) The same, in the presence of D-glucose (0.1 M) at 1 μs after the end of the pulse (3.0 mJ per pulse). c) Time profiles of ΔA at 460 and 400 nm in the presence of D-glucose (0.1 M).

sum of the quantum yields of the two intermediates was equivalent to the quantum yield of the photodegradation in water ($\Phi = 0.76$, Table 1), while the sum was remarkably lower than the photolysis quantum yield in the CD systems with high complexation percentages (Table 3).

Finally, the simultaneous presence of 2-propenol and β-CD did not substantially alter the features of the lowest energy band in the difference absorption spectrum taken with a 38 ns delay, which exhibited a maximum at 385 nm and a weaker peak at 400 nm (Figure 7, see for comparison Figure 3). This shape was maintained in the following hundreds of nanoseconds, while ΔA slightly decreased.
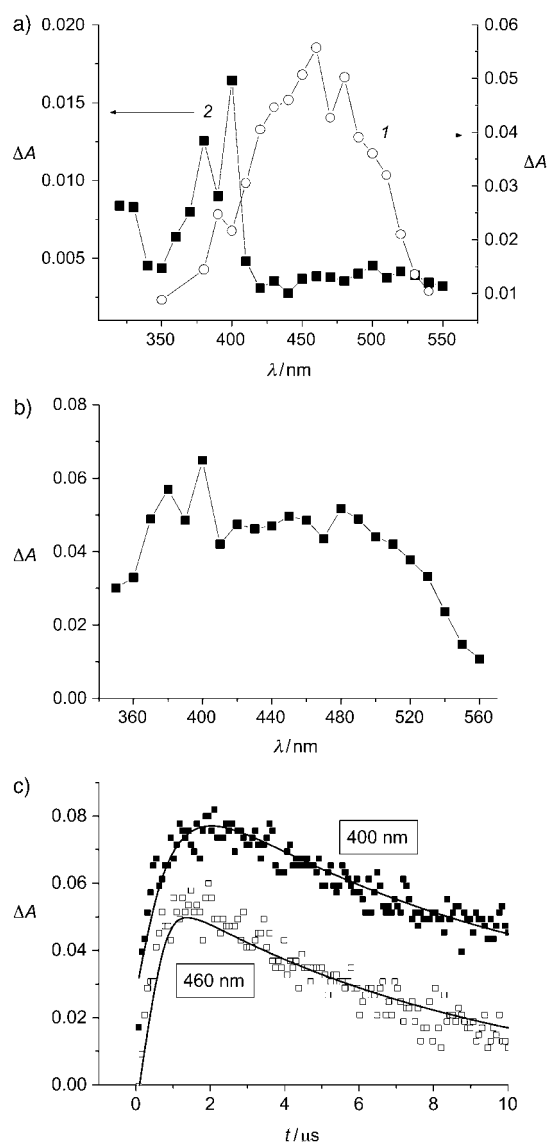
Discussion

Photochemistry of 4-chlorophenol in water: Previous work has shown that the photolysis of 2,6-dimethyl-4-chlorophenol in alcohols involves the heterolytic cleavage of the C–Cl bond in the triplet state,[10] analogously to observations with 4-chloroaniline. The 2,6-dimethyl-4-hydroxyphenyl triplet cation **^{3}2′** rapidly equilibrates with the triplet carbene **^{3}3′** (Scheme 3), as demonstrated through diagnostic reactions (the addition to allyltrimethylsilane and to oxygen, respectively). Examination of the present results leads to the conclusion that the corresponding cation **^{3}2** and carbene **^{3}3** are
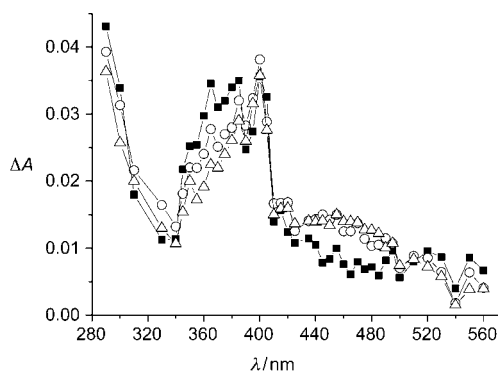
Figure 6. Difference absorption spectra of air-equilibrated water solution of **1** (1.0 mM) with β-CD (5.0 mM, 60% complex) at (■) 50 ns, (○) 430 ns, and (△) 900 ns after the end of the pulse (2.4 mJ per pulse).
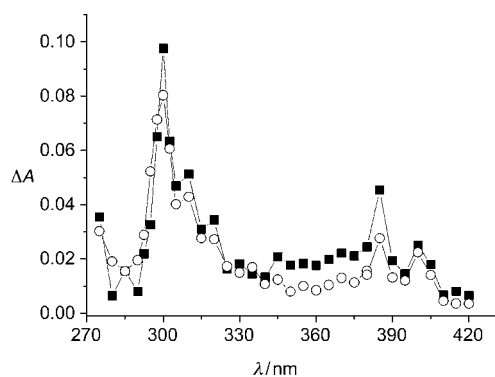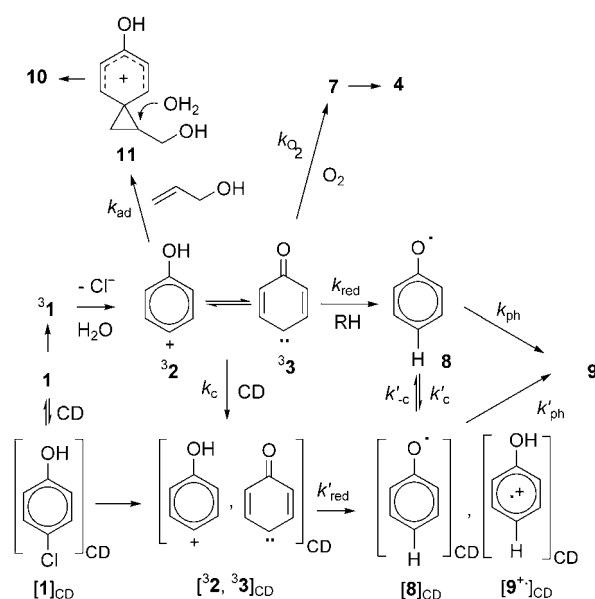

Figure 7. Difference absorption spectra of argon-flushed solution of **1** (1.4 mM) in the presence of 2-propenol (0.059 M) and β-CD (0.013 M ; ■) 38 ns, and (○) 0.8 μs after the end of the pulse (2.5 mJ per pulse).

Scheme 6. Proposed reaction mechanism for the heterolytic photolysis of **1** in the presence of cyclodextrins.

also formed in equilibrium by the photolysis of the parent 4-chlorophenol in water (Scheme 6).

The role of the former intermediate is clearly demonstrated by addition to 2-propenol (in refs. [8–10] we discussed the fact that the reaction with alkenes involves triplet phenyl cations, not oxo- (or imino-) cyclohexadienylidenes). The absorption bands in the spectrum at 38 ns after excitation (Figure 2) are attributable to carbene **^{3}3**, in agreement with results in references [5,7]. This is completely formed and thus any equilibrium is established at this stage.

According to recent calculations, cation **^{3}2** is not expected to absorb at $\lambda > 250$ nm[19] and is thus not directly accessed with our apparatus. However, this intermediate is revealed by its reaction with 2-propenol, which gives rise to a species with an intense absorption, $\lambda_{max} = 290$ nm. The rate of trapping ($k_{add} \sim k_q = 1.3 \times 10^8 \, M^{-1} s^{-1}$) is close to that determined for the addition of the 2,6-dimethyl-4-hydroxyphenyl cation to allyltrimethylsilane in alcohols ($k_{add} \sim 1–10 \times 10^8 \, M^{-1} s^{-1}$).[10] Preparative experiments show that the main product is phenylpropylene glycol (**10**). These results support the assumption that the 290 nm transient is attributable to the phenonium ion **11**, already identified in the case of the 2,6-dimethyl derivative[10] and indicated as a strongly favored adduct by calculations of the aminophenyl cation.[9] This transient un-

dergoes regioselective opening to give product **10**, owing to the favored attack by water onto the more substituted position and to the cooperative effect of the hydroxy group.

As for carbene **^{3}3**, apart from the diagnostic trapping by oxygen ($k_{O_2} = 3.5 \times 10^9 \, M^{-1} s^{-1}$),[5] the other characteristic reaction is hydrogen abstraction to form the phenoxyl radical **8** (Scheme 6, as observed with alcohols (rate constants k_{red} from $1 \times 10^6 \, M^{-1} s^{-1}$ (MeOH) to $1.9 \times 10^7 \, M^{-1} s^{-1}$ (2-butanol)).[5] D-Glucose reacts with a rate constant in the expected range ($8.5 \times 10^6 \, M^{-1} s^{-1}$). In air-equilibrated solutions containing glucose, both reactions compete to form transients **7** and **8** (Figure 5b). The sum of their formation quantum yields is equivalent to the quantum yield of consumption of **1** (Tables 1 and 3). Correspondingly, the expected mixture of products **4** and **9** is obtained in preparative experiments (Table 1). Note that in the presence of 2-propenol, some phenol is formed (Table 1). This additive also acts as a H donor, although to a minor degree, as one may expect from the lower value of k_{red} with alcohols with respect to k_{add} with alkenes.

In conclusion, in the presence of a sufficient amount of the appropriate trapping agent, the reaction can be driven, virtually entirely, either to the arylation of alkenes via the phenyl cation or to formation of benzoquinone or phenol via the carbene. The equilibrium between the two key intermediates is established within a few tens of nanoseconds in water, where these species persist in the microsecond time range, because water neither donates hydrogen nor adds, as generally observed with n nucleophiles. We have no direct evidence with regard to the position of the equilibrium; however, a comparison with the case of $\mathbf{2'} \rightleftharpoons \mathbf{3'}$ in alcohols[10] suggests that in water (more basic than methanol)[20] **3** is favored ($K_{eq} > 4$). As evidenced by Grabner,[5] the detectable intermediate mainly decays through interaction with ground

state **1** to yield dihydroxybiphenyl **6**. This reaction is now more consistently rationalized as an electrophilic substitution by phenyl cation **³2**, rather than as an addition by the carbene (note that attack of benzene by the 4-hydroxyphenyl cation has been demonstrated in organic solvents).[8, 21]

Complexation of the intermediates: As seen above, the intermediates **³2⇌³3** can be selectively quenched and, while glucose is a quencher as efficient as monohydroxylic alcohols, cyclodextrins are much more efficient (see Table 2). A quantification of the latter process requires some care, since CD efficiently complexes phenol **1** and the photochemistry involving complexed **1** must be distinguished from the photochemistry of the free phenol followed by complexation of the intermediates. Fortunately, as will be discussed below, the former reaction occurs on a shorter timescale than the latter one, thus offering a suitable time window for disentangling the two contributions. Some time-resolved spectra have been chosen to illustrate the chemistry taking place. Thus, the spectrum at 140 ns in Figure 4 (25% of **1** complexed by β-CD) indicates the formation of carbene in water at 385 nm with just a small fraction of complexed phenoxyl radical **8** at 400 nm (see below). The "initial" spectrum evolves with a time constant of ≈ 400 ns toward a spectrum that clearly shows the features of the radical **8** absorption (peaks at 385/*400* nm). Note that the reactions of the free intermediate in water contribute to the "final" spectrum because $\approx 40\%$ of it is not trapped by the CD ($k_q = 9.4 \times 10^8 \, \mathrm{M^{-1} s^{-1}}$, $k_0 = 1 \times 10^6 \, \mathrm{s^{-1}}$).

Further information is obtained by the use of the intense absorption of carbonyl oxide **7** as a sensitive probe. Thus, in Figure 6 (60% of **1** complexed by β-CD), the formation both of **7** at 460 nm (with $k_{obs} = 5 \times 10^6 \, \mathrm{s^{-1}}$) and radical **8** at 400 nm can be appreciated at 430 ns. Formation of **8** from complexed **1** is evidenced by the peak at 400 nm at 50 ns, which then increases. Although this effect is small, it is significant if considered together with the strong decrease at shorter wavelengths and provides evidence that a fraction of radicals **8** is formed parallel to **7** by competitive trapping of the free intermediate by the CD.

Thus, CDs are more efficient quenchers than D-glucose (by two orders of magnitude if the number of glucose units per CD unit is taken into account), demonstrating that inclusion in the CD cavity is involved.[22] CDs are known to complex neutral species more readily than charged species;[14] however, this makes no difference in the present case because the **2⇌3** equilibrium is established on a timescale (~ 10 ns) that is much shorter than that of complexation (~ 100 ns at CD concentrations of $\sim 10^{-2} \, \mathrm{M}$). The rate of complexation k_c is estimated to be similar to k_q on the basis of the experiments in the preformed inclusion complex, which show that $k'_{red} \geq 5 \times 10^7 \, \mathrm{s^{-1}}$ (see below).

Photochemistry of 1 with CD: As shown by Table 1, the quantum yield of dehalogenation of **1** is high and remains the same when the phenol is complexed with CD. There is no reason to believe that the photodehalogenation mechanism changes from C–Cl heterolysis via the triplet state occurring in neat water and in alcoholic media. Were this not the case, Φ should have been much lower and the triplet should have been detectable by flash photolysis, as observed with **1** in apolar solvents.[10]

Although the primary photochemical step remains the same, the final product distribution from **1** differs from neat water. Formation of *p*-benzoquinone (**4**, $\lambda_{max} = 245$ nm, see Figure 1) is nearly eliminated when **1** is complexed to a large extent and reduction to phenol **9** is the main process (Table 1). Reduction is not unexpected because the CD cavity contains easily transferable H atoms (α-hydroxyl C–H bonds) and may occur according to two mechanisms, either via **3** to give radical **8** or via **2** to give radical cation **9⁺·** (Scheme 6). The latter mechanism has been demonstrated for the dimethyl analogue in alcohols,[10] but is not operating in non-hydrogen-donating water (see below).

Some aspects deserve a comment. First, complexation of **1** by CDs inhibits trapping by either oxygen or 2-propenol. Previous work[23–25] has shown that the inclusion of phenols places the benzene ring in the inner region, while the hydroxy group is close to the secondary hydroxylic groups of the larger rim of CD molecules, as expected from the hydrophobic nature of the CD cavity. Thus, the photochemically activated C_4 atom is formed within the cavity and is not accessed by either oxygen or 2-propenol. By enlarging the cavity, namely by the use of β-CD instead of α-CD, makes the restriction less severe as supported by the increasing yields of **4** and **10** (see Table 1), a trend further extended by the results observed with γ-CD (not reported here).

Second, time-resolved experiments give a detailed insight into the process. In contrast to neat water, no carbene **³3** is detected on flashing solutions containing more than 80% of complexed **1** (see Figure 4 and Figure 5), where the earliest transient spectrum (long-wavelength maxima at 385 and 400 nm), similar to that with glucose or alcohols, is attributed to radical **8**. This is formed in the cavity with the rate $k'_{red} \approx k_{obs} \geq 5 \times 10^7 \, \mathrm{s^{-1}}$, in agreement with the lack of interference by external agents. Note that under these conditions, the more intense peak lies at 385 nm rather than at 400 nm, the reverse of what is observed both in water and in apolar solvents,[17] pointing to a specific interaction of the phenoxyl radical **8** with the CD. Radicals **8** partly react within the cavity (**8→9**, $k_{obs} = k'_{ph} \approx 10^7 \, \mathrm{s^{-1}}$). As clearly observed with β-CD (see Figure 3), the spectral profile changes and makes 400 nm the more intense peak in 140 ns. This is rationalized with respect to the contribution by the fraction of radicals that have escaped into the aqueous bulk with a rate constant $k'_{-c} \approx 10^7 \, \mathrm{s^{-1}}$.[26,27] Thus, the CD structure governs the fate of radical **8**, which can either abstract a further H from the cavity or diffuse in solution. In the latter case, it can be reduced through a slower path, presumably by interaction with the primary rim of the CD (k'_c) because reduction in neat water (k_{ph}) is unlikely.

Third, the sum of the quantum yields of the transients **7** and **8** (see Table 3) is equivalent to Φ_r in the presence of D-glucose, whereas it is $\approx \frac{1}{2}$ and $\frac{1}{3}$ of Φ_r for β-CD-and α-CD

complexed with **1**, respectively, and corresponds to the yield of **8**. Because the conversion of carbene **3** to radical **8** within the cavity is presumably complete and the disappearance of **8** by reduction to **9** is not faster than its formation (see above), a fraction of the initially formed aryl cation must undergo H transfer from the CD at a rate comparable to that at which deprotonation to **3** and formation of **8** occur ($\geq 5 \times 10^7$ s^{-1}). Production of **9** directly from **2** via the radical cation **9$^{+\cdot}$** in the presence of CD is indeed supported by the presence both of a shoulder at λ = 420–430 nm in the spectra of Figure 4 and Figure 5 and of the absorption tail at λ = 510–550 nm in Figure 6, which can be assigned to the radical cation, a species endowed by a large absorption band in the 380–550 nm region.[10, 28]

Conclusion

The present study demonstrates that the 4-hydroxyphenyl cation **³2** and carbene **³3** are in equilibrium and are relatively persistent in water. Specific reagents can selectively trap these intermediates. Thus, water is a suitable solvent to conduct reactions involving either one of such highly activated species, which are smoothly generated under photochemical conditions, in particular for synthetically appealing cationic arylation of alkenes and, reasonably, of other π nucleophiles.[29]

On the other hand, cyclodextrins efficiently scavenge and reduce the intermediates. When cyclodextrin concentrations are chosen in such a way as to associate more than 80 % of ground state **1**, the largest fraction of the chlorophenol is reduced within the cavity and none of the above traps interfere with the reduction. The large time-window involved in the reaction in water (10 ns scale, photochemical fragmentation and protic equilibrium; 100 ns, trapping by oxygen and alkenes; 1 μs, reaction with the starting material) is shortened to a few tens of nanoseconds.

The high reductive power of the CD towards both the aryl cation and the carbene disfavors the use of CDs as reaction vessels for bimolecular processes, although an efficient coinclusion of the trap could allow a guest–guest process to compete efficiently with a reaction with the CD itself. In the present study, the high solubility of 2-propenol in water prevents such condition being achieved.

Experimental Section

General: 4-Chlorophenol (**1**) and 2-propenol were obtained from Aldrich. α-CD and β-CD from SERVA (research grade) were used as received. Water was purified by passing it through a Millipore MilliQ system.

The UV absorption spectra were recorded with a Perkin Elmer 320 spectrophotometer. Circular dichroism spectra were obtained with a Jasco J-710 dichrograph.

Measuring the complexation by CD: Circular dichroism spectra of 4-chlorophenol in water were recorded by titrating with cyclodextrins at 8–10 different concentrations and by subtracting from each of them the in-

trinsic signal of the corresponding cyclodextrin solution. The intensity of the induced signal was a function of the CD concentration and was analyzed by means of a 1:1 association model described by a nonlinear equation.[13]

Monitoring the photoreaction by UV: The time course of the photodehalogenation was followed by variations in the UV absorption of 2-mL samples of 3.14×10^{-4} M solutions of **1** irradiated at 282 nm in a 1 cm cell. The irradiation setup consisted of a high-pressure mercury lamp (Osram HBO, 200 W) coupled with a high-intensity Bausch&Lomb grating monochromator (1350 grooves mm^{-1}, blazed at 300 nm) with slits of 3 mm (bandwidth 18 nm). The intensity of the incident light was $\approx 1 \times 10^{14}$ photons s^{-1}.

Monitoring the photoreaction by HPLC and quantum yield measurements: Quantum yield measurements were carried out with an optical bench fitted with a focalized high-pressure mercury arc (150 W) and an interference filter (transmission maximum at 281 nm). 1.5×10^{-3} M solutions of **1** in spectrophotometric cells were used. The course of the reaction was monitored by HPLC (AQUASIL1 C18 (250×4.6 mm) column, MeCN/water (40:60), flux 1 mL min^{-1}) with UV detection at λ = 270 nm. The conversion was limited to < 20 %. The conversion of the starting material was linear with time within this limit and beyond in the presence of additives, while in neat water, the rate of reaction rapidly dropped for conversions of < 10 %. This was attributed to the formation of photoproducts strongly absorbing at the exciting wavelength. Reliable measurements could only be obtained in this case by the use of 7×10^{-4} M solutions.

Preparative photolysis: A solution of 4-chlorophenol (100 mg, 0.78 mM) and 2-propenol (750 μL, 15 mM) in water (15 mL) was poured into a quartz tube. The tube was flushed with argon for 15 min, capped, and irradiated with six phosphor-coated lamps (15 W, center of emission λ = 310 nm). After 16 h, the reagent had been completely converted (HPLC) and a single product accounted for ≈ 80 % of the material (as determined by comparison with a weighted solution of **10**, see below). The solvent was evaporated under low pressure and the residue chromatographed on silica gel to give 32 mg (25 %) of the main product. This was recognized as 3-(4-hydroxyphenyl)-1,2-propandiol, based on the spectroscopic characteristics and a comparison with reported data.[30, 31] ^{1}H NMR (CDCl$_3$): δ = 2.67 (AB part of an ABX signal, 2H, J(A,B) = 15 Hz), 3.47 (AB part of an ABX signal, 2H, J(A,B) = 12.5 Hz), 3.78 (X part of the previous signals, 1H), 6.75 (2H) and 7.07 (AB quartet, 4H); ^{13}C NMR (CDCl$_3$): δ = 38.6 (CH$_2$), 65.0 (CH$_2$), 73.3 (CH), 114.6 (CH), 129.3, 130.0 (CH), 155.2 ppm; IR (melt): $\tilde{\nu}$ = 3300 cm^{-1}; elemental analysis (%) calcd for C$_9$H$_{12}$O$_3$: C 64.27, H 7.19; found: C 63.9, H 7.3.

Flash photolysis: Transient absorption spectroscopy was carried out on a setup for nanosecond absorption measurements described previously.[32] The minimum response time of the detection system was ≈ 2 ns. The laser beam from a JK-Lasers Nd-YAG, operated at λ = 266 nm, pulse width 20 ns FWHM, was focused on a 3 mm high and 10 mm wide rectangular area of the cell, and the first 2 mm in depth were analyzed with a right-angle geometry. The incident pulse energies used were < 17 mJ cm^{-2} (5 mJ per pulse). The bandwidth used for the transient absorption measurements was typically 2 nm (0.5 mm slit width). The spectra were reconstructed point-by-point from time profiles taken every 5–10 nm. The sample absorbance at 266 nm was typically 0.5–1 over 1 cm. Oxygen was removed from the water by vigorously bubbling the solutions with a constant flux of Ar, previously passed through an aqueous trap to prevent evaporation of the sample. The solution, in a flow cell of 1 cm optical path, was renewed after each laser shot. The temperature was 295 ± 2 K. The detection system was perturbed from 290 nm to 380 nm by the emission of **1**, generated by the laser excitation. These problems were minimized by the use of neutral density filters at the entrance slit of the monochromator and by pulsing the 150 W high-pressure Xe lamp with a high current (~200 mA for 1 ms) to increase the intensity of the analyzing light. In spite of this, transient spectra in this wavelength region were not significant before 20–35 ns from the end of the pulse. The absorption signals were acquired and processed with a homemade program and Asyst 3.1 (Software Technologies, Inc.). Nonlinear fitting

procedures by the least-square method and χ^2 and distribution of residuals were used to judge the goodness of the fit.

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