A nanosecond laser flash photolysis study of aqueous 4-chlorophenol

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Abstract

The mechanism of the aqueous photoreaction of 4-chlorophenol was studied by nanosecond laser flash photolysis. The carbene 4-oxocyclohexa-2,5-dienylidene is formed from the chlorophenol by loss of HCl. This species reacts efficiently with oxygen to form 1,4-benzoquinone-O-oxide which subsequently yields 1,4-benzoquinone. The carbene also undergoes reaction with water and coupling reactions to produce 1,4-hydroquinone and polyhydroxybiphenyls respectively.

Keywords: Laser flash photolysis; 4-Chlorophenol

1. Introduction

The chlorophenols are a fairly simple class of molecules which are widely spread throughout the environment due to their discharge from industrial plant and by current water treatment methods which often involve the use of chlorine. In aqueous solution, they are exposed to UV and visible radiation from the sun, and it is believed that, particularly for the higher chlorophenols [1–3], photochemical mechanisms (direct excitation and sensitization) play a major role in determining their fate. Compounds such as 4-chlorophenol (4-CP, 1) are also of interest as models of the photochemical reactivity of aromatic organochlorine compounds in aqueous media, e.g. in a number of recent studies involving advanced oxidation processes [4].

In aqueous solution, 4-CP undergoes a range of photochemical reactions depending on the presence of oxygen, the concentration of the chlorophenol and the pH. At neutral or acidic pH values, where 4-CP is not ionized, and in the presence of oxygen, the principal photoproduct is 1,4-benzoquinone (2) [5–8]. A range of minor products are also observed, including 1,4-hydroquinone (3), 2-hydroxy-1,4-benzoquinone (4) and several polyhydroxybiphenyls [5,7]. In degassed solution, Boule and coworkers [5,7] found that the products based on 1,4-benzoquinone (2 and 4) were absent, whereas other workers [6,8] concluded that their yields were merely reduced. We have re-examined the reaction in rigor-

ously degassed solution and agree with Boule and coworkers that, in the absence of oxygen, the benzoquinones are completely absent from the mix of photoproducts [9]. It therefore seems that the second oxygen atom in products 2 and 4 originates from a molecule of dioxygen. Interestingly, the quantum yield of consumption of 4-CP, which has been variously reported as 0.25 [5], 0.4–0.5 [10] and 0.44±0.1 [11], is reported to be independent of the oxygen and chlorophenol concentrations and the pH [5,10]. However, the more recent work of Grabner and coworkers [12,13] indicates that the quantum yield is dependent on the concentration of 4-CP.

Mechanistic interpretations of these observations have all assumed homolysis of the ring-chlorine bond to yield a 4-hydroxyphenyl radical. This reacts with molecular oxygen to yield a peroxy radical, which then undergoes further reaction(s) to result finally in 1,4-benzoquinone (Scheme 1). During the course of the reaction, oxidation of the aromatic ring must occur to produce the 1,4-benzoquinone. In their earlier work, Boule et al. [5] achieved this through disproportionation of two semiquinone radicals. However, a variety of possible mechanisms for the formation of 1,4-benzoquinone have been explored in the more recent work of Oudjehani and Boule [7]. The minor photoproducts are assumed to arise from either photohydrolysis (1,4-hydroquinone) or coupling reactions between the radical intermediates and a molecule of 4-CP or one of the photoproducts.

At alkaline pH, where 4-CP is ionized ($pK_a = 9.4$) to 4-chlorophenolate, the same photoproducts are observed but in different relative amounts [5,8,9]. The yields of 2 and 3

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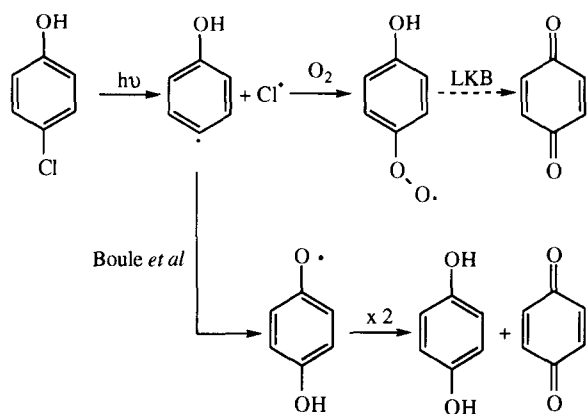
Scheme 1. Mechanisms of the aqueous photoreactions of 4-CP according to Lipczynska-Kochany and Bolton [6] (LKB) and Boule et al. [5].

decrease with increasing pH, until at pH 12 no **2** and very little **3** is observed. The yield of **4** rises with pH. These observations are not unexpected given the known instability of both **2** and **3** at high pH. Again, the mechanisms yielding these products are not well understood.

Continuing our work on the photochemistry of this system, we have undertaken a nanosecond flash photolysis study of the transient species observed from 4-CP in aqueous solution. Whilst this was underway, we became aware of the work of Grabner and coworkers [12,13].

2. Experimental details

4-CP was obtained from Aldrich Chemicals Ltd. and was sublimated (40–45 °C, 11 mbar) before use. Water was distilled and deionized. Alkaline and acidic pH values were obtained by the addition of the appropriate amount of Analar hydrochloric acid (BDH Ltd.) or sodium hydroxide (Aldrich Chemicals Ltd.). Chloride levels were adjusted with Analar sodium chloride solution (BDH Ltd.). Degassing (when required) was performed by a series of freeze–pump–thaw cycles.

Absorption spectra were recorded on a Hewlett-Packard model 8452A diode-array spectrometer. Nanosecond flash photolysis was carried out with an HY200 Nd:YAG laser (Lumonics). The excitation wavelength was 266 nm. The monitoring source was a 300 W xenon arc lamp (Optical Radiation Corporation) (unpulsed). Detection was via a Hamamatsu R928 photomultiplier tube through an f/3.4 grating monochromator (Applied Photophysics Ltd.). Signals from the photomultiplier tube were digitized with a 2432A digital oscilloscope (Tektronix) and the data were transferred via a GPIB interface for analysis to an IBM-compatible PC. Opening of the shutters for the arc lamp and the laser was computer controlled through a DT2808 D/A interface card (Data Translation). The timing of the system was controlled via a home-built analogue delay generator [14]. For most of

the measurements, a concentration of 1.0×10^{-3} mol dm^{-3} was used, which gives an absorbance at 266 nm of approximately 0.4. Samples were only subjected to a single flash before they were replaced by fresh solution.

3. Results

3.1. 4-CP in neutral aqueous solution

Nanosecond laser flash photolysis (at 266 nm) of a 1×10^{-3} mol dm^{-3} aerated aqueous solution of 4-CP reveals transient absorption in the wavelength range 340–550 nm, 340 nm being the lowest detection wavelength available on the equipment used. The transient absorption decays completely within a few tens of microseconds. Transient absorption traces were measured at 10 nm intervals on a time scale of 0–10 μs and were analysed to yield the transient spectra shown in Fig. 1. Initially, there is an absorption maximum at 370 nm. At later times, a second absorption band, situated in the visible–UV with a peak at approximately 460 nm, grows in and subsequently decays. Absorption in the region 340–370 nm remains approximately constant for the first few microseconds following excitation and then decays. Thus two transient species are detected in these experiments. The first band shows a maximum at 370 nm and is produced immediately (on a time scale of less than a few tens of nanoseconds) after excitation, whereas the second transient ($\lambda_{max} = 460$ nm) absorbs throughout the UV and visible region from 550 to 340 nm and exhibits a clear "grow-in" when monitored at visible wavelengths where its precursor does not absorb.
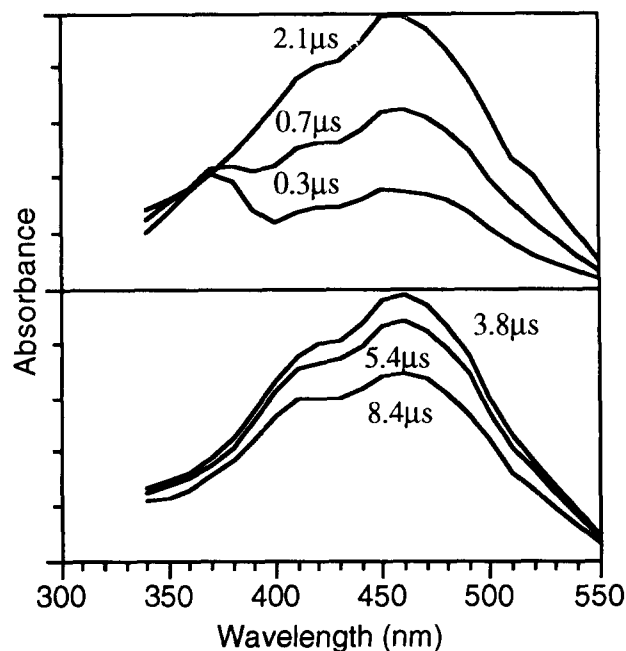

Fig. 1. Transient absorption spectra of 4-CP (10^{-3} mol dm^{-3}) in aerated water at various delay times. Absorbance range for each spectrum, 0–0.1.
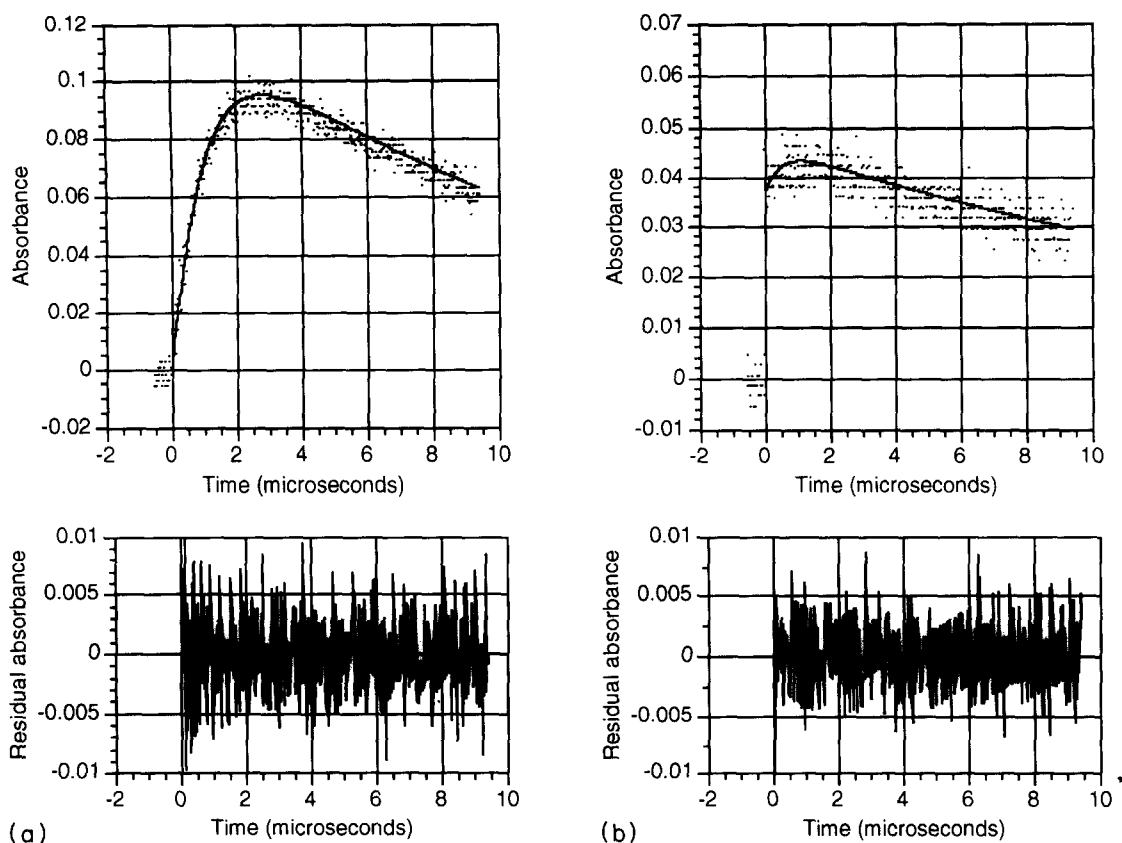
Fig. 2. (a) Transient absorption of 4-CP in neutral, aerated aqueous solution monitored at 470 nm, together with biexponential fitted curve and residuals. (b) Transient absorption of 4-CP in neutral, aerated aqueous solution monitored at 370 nm, together with biexponential fitted curve and residuals.

Analysis of the individual kinetic traces reveals two separate types of behaviour. Above 400 nm, the traces are typified by that shown in Fig. 2(a) in that a clear rise and decay are found. Computer convolution of the experimental traces to a biexponential function of the type

$$\text{Absorbance} = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \tag{1}$$

gives very acceptable fits (as shown by the full line in Fig. 2(a)) with $A_1 = -A_2$, $k_1 = (1.0 \pm 0.1) \times 10^6$ s^{-1} and $k_2 = (8.5 \pm 1.0) \times 10^4$ s^{-1}. On a longer time scale, the transient absorption returns to the baseline and rate constant values identical to those quoted above are obtained from an analysis of the curves.

Below 400 nm, where both transients absorb, the traces can be fitted using the same time constants. A typical example is shown in Fig. 2(b). This supports the suggestion of an initially formed transient which decays to form a second transient, which then itself decays. The spectra presented in Fig. 1 and the kinetic fits above 400 nm suggest a parent/daughter relationship between the two transients. Thus, below 400 nm, the kinetic traces are a combination of the decay of the first transient species together with the rise and subsequent decay of the second transient, i.e. Eq. (1) still applies but with $A_1 \neq -A_2$ and $|A_1| < |A_2|$. This is found to be the case, but with the variance of the fits being greater than for the longer wavelengths due to the lower absorbance changes which are observed at the shorter wavelengths.

Both k_1 and k_2 exhibit some concentration dependence. Aqueous aerated solutions of 4-CP in the concentration range $(0.1–3.0) \times 10^{-3}$ mol dm^{-3} were excited at 266 nm with the nanosecond laser and the absorption changes were monitored at 470 nm where both rate constants are easily calculated as shown previously. The results of these measurements are shown in Figs. 3(a) and 3(b), where it can be seen that both rate constants increase with concentration in the range 10^{-4}–10^{-3} mol dm^{-3}. Above 10^{-3} mol dm^{-3}, they appear to decrease again; the reason for this is not obvious and we are undertaking further work at these higher concentrations. Best straight line fits to the data between 10^{-4} and 10^{-3} mol dm^{-3} yield the relationships

$$k_1 = 1.6 \times 10^8 [\text{4-CP}] + 9.0 \times 10^5 \text{ s}^{-1} \tag{2a}$$

$$k_2 = 3.5 \times 10^7 [\text{4-CP}] + 5.7 \times 10^4 \text{ s}^{-1} \tag{2b}$$

These two straight lines are shown superimposed on the experimental data in Figs. 3(a) and 3(b).

Saturation of a 1.0×10^{-3} mol dm^{-3} aqueous solution of 4-CP with oxygen yields transients with broadly the same characteristics as those seen in aerated solution. As shown in Fig. 4, two transients with spectra essentially identical to those in aerated solution are observed. The intensity of the first transient (absorbing below 400 nm) is similar to that in aerated solution, but the second transient is approximately twice as intense in oxygen-saturated solution. Kinetic anal-

(a)

(b)
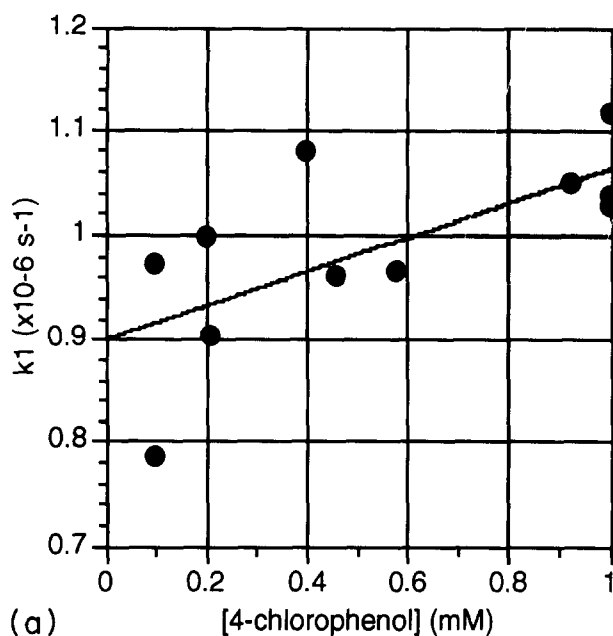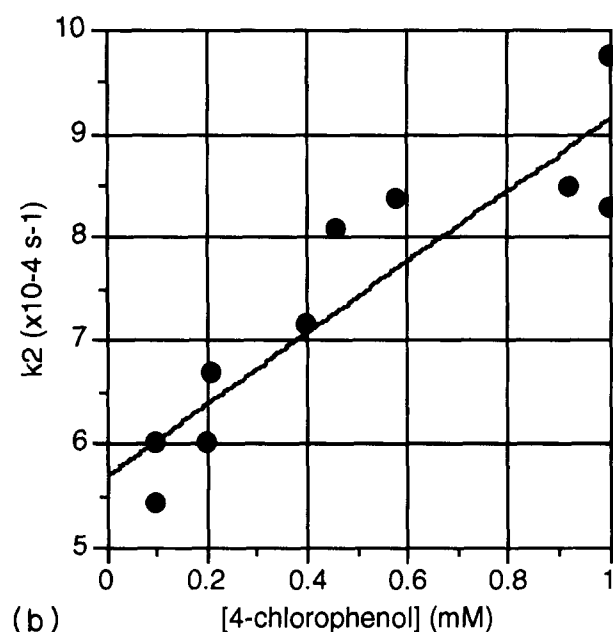
Fig. 3. Variation of k_1 (a) and k_2 (b) with 4-CP concentration.

ysis of the transient traces of absorbance vs. time has broadly the same outcome as in aerated solution. Above 400 nm, the data can be adequately fitted by Eq. (1) with $A_1 = -A_2$, $k_1 = (3.0 \pm 0.3) \times 10^6$ s^{-1} and $k_2 = (9.5 \pm 1.0) \times 10^4$ s^{-1}. A typical experimental profile, together with the computed fit, is shown in Fig. 5.

Comparison of the pairs of rate constants obtained in aerated and oxygen-saturated solution reveals that k_1 is approximately trebled (from 1.0×10^6 s^{-1} to 3.0×10^6 s^{-1}), whereas k_2 increases by 10% (8.5×10^4 s^{-1} to 9.5×10^4 s^{-1}). The rate constant k_1 may be broken down into two contributions: the intrinsic decay constant for the first transient (k_{1a}) and the rate constant for reaction with oxygen (k_{1b}) i.e.
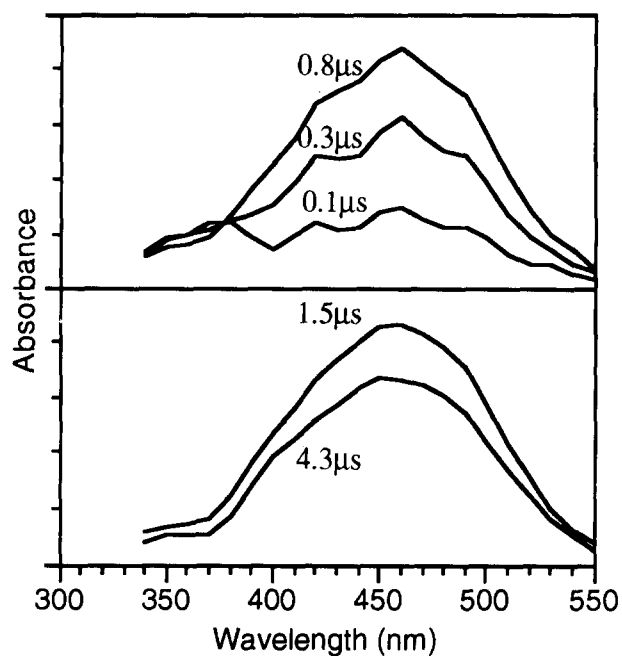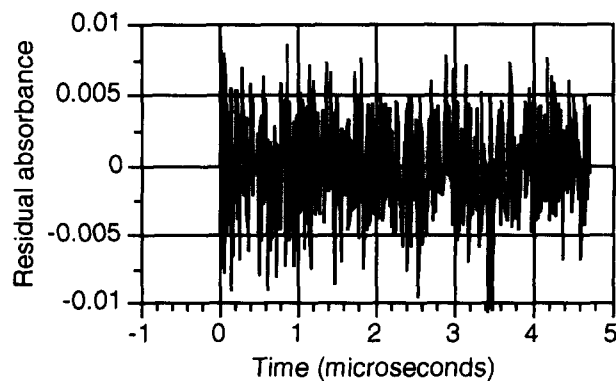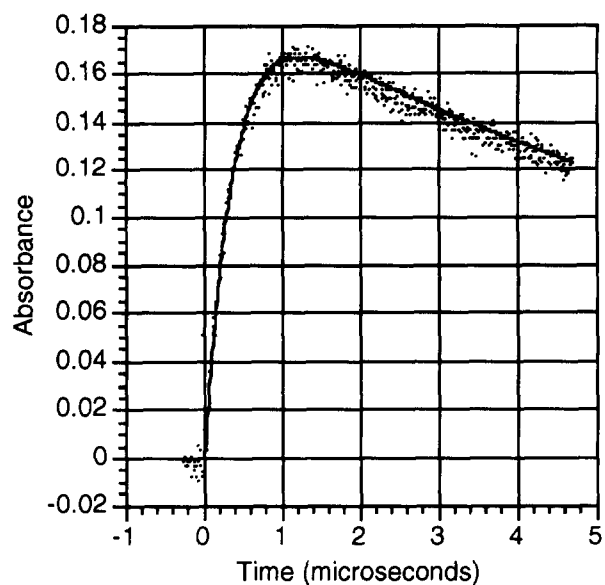

Fig. 4. Transient absorption spectra of 4-CP (10^{-3} mol dm^{-3}) in oxygenated water at various delay times. Absorbance range for each spectrum, 0–0.2.

Fig. 5. Transient absorption of 4-CP in neutral, oxygenated aqueous solution monitored at 470 nm, together with biexponential fitted curve and residuals.
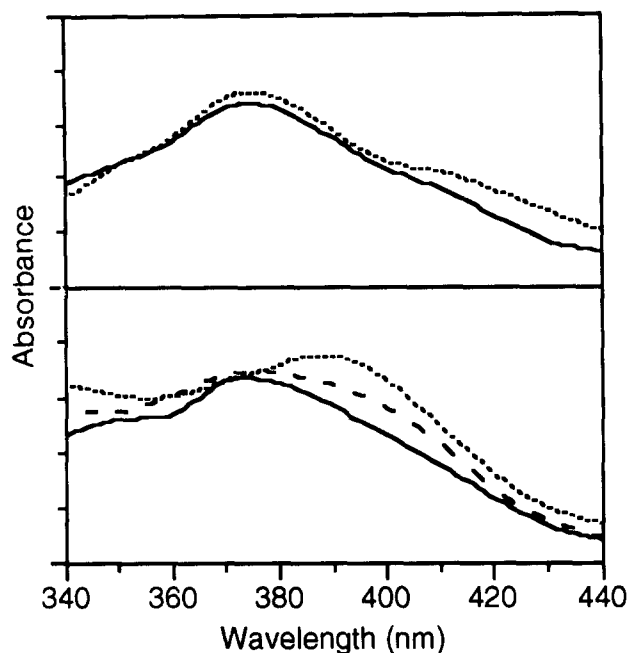
Fig. 6. Transient absorption spectra of 4-CP (10^{-3} mol dm^{-3}) in neutral, degassed water at delay times of 0.3 μs (full line, top spectrum), 0.9 μs dotted line, top spectrum), 2.1 μs (full line, bottom spectrum), 4.5 μs broken line, bottom spectrum) and 8.2 μs (dotted line, bottom spectrum). Absorbance range for each spectrum, 0–0.04.

$$k_1 = k_{1a} + k_{1b}[O_2] \qquad (3)$$

When the values of k_1 determined in aerated and oxygen-saturated solution are inserted into this equation, together with the corresponding oxygen concentrations (2.58×10^{-4} mol dm^{-3} and 1.29×10^{-3} mol dm^{-3} respectively at 25 °C), the calculation yields $k_{1a} = (5.4 \pm 1.0) \times 10^5$ s^{-1} and $k_{1b} = (1.9 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1}.

In degassed (freeze–pump–thaw) aqueous solutions of 4-CP (1.0×10^{-3} mol dm^{-3}), transient absorption is only observed in the region 340–450 nm. Initially, the spectrum shows λ_{max} at 380 nm (Fig. 6) which shifts within 10 μs to give a characteristic spectrum of a longer lived transient which peaks at 400 nm (see the trace at 8.2 μs delay). The lifetime of the long-lived transient in degassed solution has proved difficult to characterize. At present, it appears to decay by first-order kinetics with a rate constant of approximately 30 ± 20 s^{-1}. Analysis of the individual kinetic traces in degassed solution was performed on the basis of a function of the form

$$\text{Absorbance} = A \exp(-k_3 t) + C \qquad (4)$$

The constant (C) represents the (effectively constant on this time scale) absorbance of the long-lived species. The values of k_3 obtained vary quite widely in the range 3.0×10^5 to 7.0×10^5 s^{-1}, reflecting a small change in absorption superimposed on a higher "baseline" absorption. However, the k_3 values are certainly in the range expected on the basis of the k_{1a} value (($5.4 \pm 1.0) \times 10^5$ s^{-1}) determined earlier.

The addition of various amounts of chloride ion (0–3 mol dm^{-3} in the form of sodium chloride) to solutions of 4-CP (1.0×10^{-3} mol dm^{-3}) in neutral, aerated water affects the transients observed. Biexponential kinetics (Eq. (1)) are still applicable with equal and opposite pre-exponential factors. However, the sizes of the pre-exponential factors (which are related to the yield of the transient) clearly decrease with increasing chloride concentration. The values of k_1 and k_2 lie largely within the uncertainty values placed on these rate constants.

3.2. 4-CP in acidic aqueous solution

The addition of protons (in the form of very dilute hydrochloric acid) appears to accelerate the decay of both transient species observed in aerated aqueous solution. The kinetics of the rise and decay of the transient at 470 nm were monitored as a function of the proton concentration in the range (0–2) $\times 10^{-3}$ mol dm^{-3}. The resulting rate constants are plotted as a function of [H$^+$] in Fig. 7. Both k_1 and k_2 appear to increase roughly linearly with proton concentration in the range used, suggesting that both transients are quenched by protons with rate constants of $(1.1 \pm 0.2) \times 10^9$ dm^3 mol^{-1} s^{-1} and $(4.4 \pm 1.0) \times 10^8$ dm^3 mol^{-1} s^{-1} for the first and second transients respectively.

3.3. 4-CP in alkaline aqueous solution

Nanosecond laser flash photolysis (at 266 nm) of a 1.0×10^{-3} mol dm^{-3} aerated aqueous solution of 4-CP containing 10^{-2} mol dm^{-3} sodium hydroxide (i.e. at approximately pH 12.0) reveals transient absorption principally between 340 and 440 nm. Transient absorption spectra recorded at various delay times after the excitation flash are shown in Fig. 8. Here, it can be seen that the strongest absorption band is centred around 400 nm, which does not decay on the time scale used. There is evidence of further transient absorption in the region of 370 nm and in the 400–500 nm wavelength range. These bands are weak and decay within
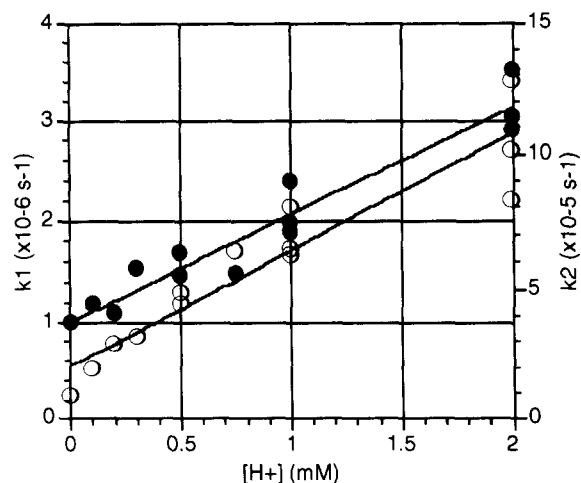

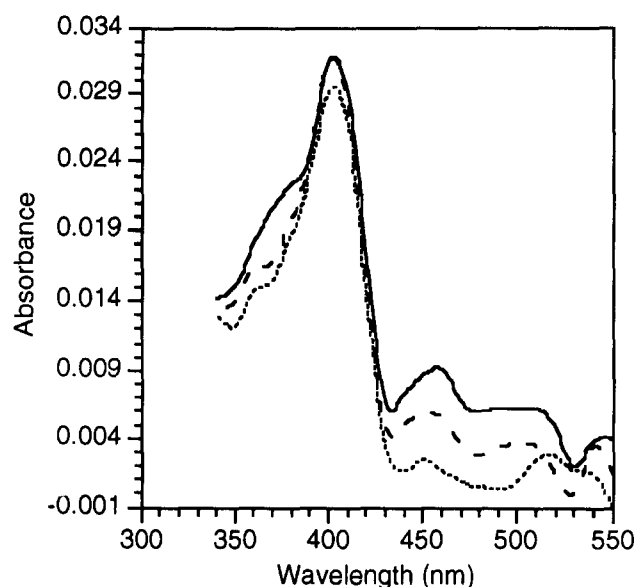Fig. 7. Effect of [H$^+$] on rate constants k_1 (O) and k_2 (●).

Fig. 8. Transient absorption spectra of 4-CP (10^{-3} mol dm^{-3}) in aerated water (pH 12) at delay times of 0.3 μs (full line), 1.5 μs (broken line) and 8.6 μs (dotted line).

Fig. 9. Transient absorption spectra of 4-CP (10^{-3} mol dm^{-3}) in oxygenated water (pH 12) at delay times of 0.3 μs (full line), 0.9 μs (broken line) and 8.6 μs (dotted line).

approximately 10 μs. When the solution is saturated with oxygen, some enhancement of absorption above 420 nm is observed (Fig. 9, see later), which indicates that the weak bands observed in aerated solution are real. The weakness of the bands either side of the main band makes kinetic analysis difficult, but we can conclude from our kinetic analyses that the weak bands shown in Fig. 8 decay with rate constants of 10^6 s^{-1} or above.

Saturation of the solution with oxygen has very noticeable effects on the transient absorption spectra (Fig. 9). The main band observed in aerated solution is still in evidence, but is present with reduced intensity. Absorption in the 400–550 nm region is greatly enhanced and the spectrum appears to be similar to that observed in this region at neutral pH. There may also be some enhancement of the transient absorption below 400 nm which is superimposed on the 400 nm band. Analysis of the kinetic traces reveals that, at 400 nm and above, the traces are adequately fitted by a single-exponential decay with an average rate constant of $(1.1 \pm 0.2) \times 10^6$ s^{-1}. If the transient observed above 440 nm is the same as that observed in neutral solution, the decrease in lifetime from some 11 μs to 500–900 ns is presumed to represent reaction with hydroxyl ions with a rate constant of $(1.0–2.0) \times 10^8$ dm^3 mol^{-1} s^{-1}.

At shorter wavelengths, the transient decay profiles are adequately fitted by Eq. (4), i.e. an exponential decay superimposed on a baseline absorption. A first-order rate constant of $(1.8 \pm 0.4) \times 10^6$ s^{-1} is obtained, which is not inconsistent with that determined for the decay above 400 nm. In the light of the results obtained at 440 nm and above, it is not possible to decide whether or not this transient absorption is due to a different chemical species to that causing the higher wavelength absorption.
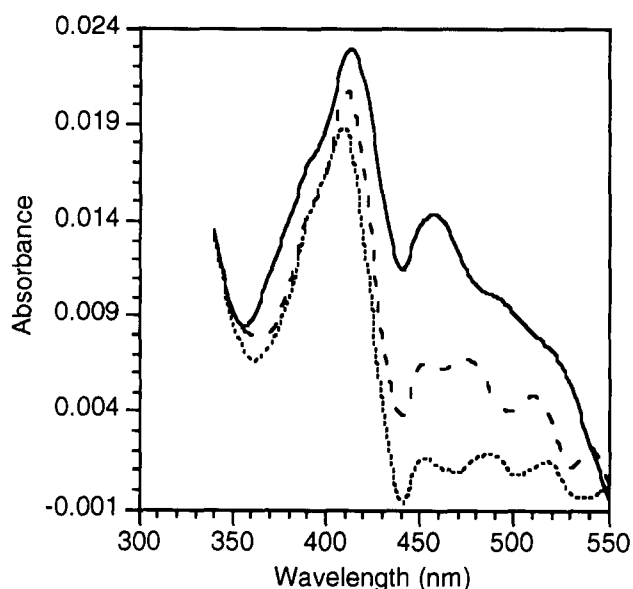
4. Discussion

The photochemistry of 4-CP in aqueous solution is complex. A variety of photoproducts have been identified both in our work and in the literature, the yields of which are dependent on the pH, concentration and presence of molecular oxygen. Indeed, the latter clearly plays a major role in determining the photochemical mechanism. In neutral, aerated or oxygenated solution, the major photoproduct is 1,4-benzoquinone, whereas this compound is completely absent in degassed solution. The second oxygen atom in 1,4-benzoquinone is therefore assumed to originate from a molecule of dioxygen. Our nanosecond flash photolysis study suggests that there are two transient species observable on a time scale of greater than 100 ns. The lifetime of the first transient is approximately 1 μs in aerated solution and some 330 ns in oxygen-saturated solution. The kinetics of the second transient are relatively unaffected by the oxygen concentration. In degassed solution, our nanosecond flash photolysis experiments show clearly that the second transient species is not formed, and we therefore conclude that the first transient is likely to be that which reacts with molecular oxygen to form a species which eventually leads to 1,4-benzoquinone.

Very recently, Richard and Grabner [12] have proposed that the mechanism for the photolysis of 4-CP in aqueous solution involves the formation of a carbene, which either reacts with molecular oxygen to yield 2 or undergoes reaction with the solvent or a second molecule of 4-CP. They suggest that this carbene, 4-oxocyclohexa-2,5-dienylidene (5), is formed from 4-CP by loss of, firstly, Cl$^-$ and then H$^+$ (Scheme 2(a)). This mechanism has a parallel in the photochemistry of 2-chlorophenol [5,10,15], 2-bromophenol and 1,2-benzoquinone-diazide [16], where 6-oxocyclohexa-2,4-dienylidene is believed to be the precursor to the forma-
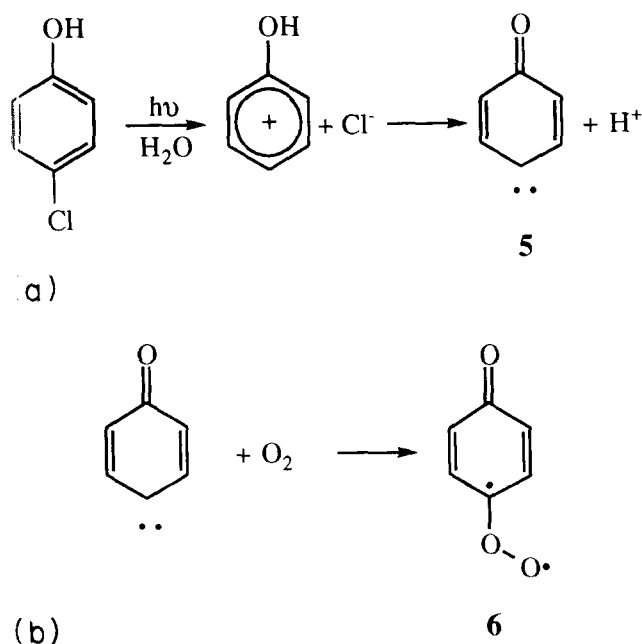
Scheme 2. (a) Formation of 4-oxocyclohexa-2,5-dienylidene (5) from 4-CP in aqueous solution. (b) Reaction of 5 with molecular oxygen.

tion of a ketene which then hydrates to give 1,3-cyclopentadienyl-1-carboxylic acid.

Some of the properties of 5 are known, since it has been prepared in inert solvents or low-temperature matrices by photolysis of 4-diazocyclohexa-2,5-dienone [17,18]. 5 exhibits absorption features at 290 nm (strong), 379 nm (medium) and 530 nm (weak) in an argon matrix and is reported to have a lifetime of 1.65 μs in Freon-113 [18]. It has a triplet ground state and readily reacts with molecular oxygen to produce p-benzoquinone-O-oxide (6, Scheme 2(b)) which absorbs throughout a large portion of the visible spectrum peaking around 470 nm (in Freon-113). The spectrum for this species, reported by Arnold et al. [18], is in good agreement with the second, longer lived transient given in Fig. 1, and we therefore believe that the second transient observed by laser flash photolysis is 6. We further conclude that the first transient observed is 5, since it is clearly the precursor of 6 and reacts strongly with molecular oxygen. Grabner et al. [13] report a spectrum for 5 which peaks at 250, 290, 370 and 384 nm in water. Their spectral range is wider than ours, but their observations are in complete agreement with those presented here. They report a rate constant for the reaction of 5 with oxygen of 3.5×10^9 dm^3 mol^{-1} s^{-1}, which compares well with our value of $(1.9 \pm 0.4) \times 10^9$ dm^3 mol^{-1} s^{-1} and with the rate constant measured by Arnold et al. [18] of 2.9×10^9 dm^3 mol^{-1} s^{-1} (in Freon-113). In the absence of molecular oxygen, 5 is calculated (k_{1a}) to have a lifetime of approximately 2 μs in water. Unfortunately, it has proved difficult to confirm this value in degassed solution due to the weakness of the transients produced and the spectral overlap between them. This compares with lifetimes of approximately 1 μs and 330 ns in aerated and oxygen-saturated water respectively.

On the basis of these lifetimes, it follows that, if all the oxygen quenching is due to reaction, in aerated solution half of 5 should react with molecular oxygen to produce 2 rising to some 82% in oxygen-saturated solution. This also assumes that 2 only arises via the direct reaction of 5 with molecular oxygen. It is also possible that one or more of the intermediates in the reaction of 5 by other routes, amongst which will be the reaction with water to produce 3 and with a second 4-CP molecule to produce coupling products, could react with oxygen to produce 2. Steady state photolysis of 4-CP in neutral water reveals 2 to be the dominant photoproduct in both aerated and oxygen-saturated solution. In aerated solution, 1,4-hydroquinone is also detected immediately during photolysis, whereas in oxygen-saturated solution this photoproduct does not appear until approximately 20% of the 4-CP has reacted [8]. The quantum yield for the disappearance of 4-CP, however, is the same under both sets of conditions. Later in the photolysis we find that the yield of 2 is approximately the same (approximately 75% of the reacted 4-CP [8,9,11]) for both aerated and oxygen-saturated solution. This yield agrees well with the calculated fate of 5 in oxygen-saturated solution, but fails to take into account the fact that the relative amounts of products formed during steady state photolysis may not truly reflect the photochemistry of 4-CP. 2 is itself photoreactive in water [19] and 3 (as well as other photoproducts) may be subjected to atmospheric oxidation and other ground and excited state chemistry which leads to the formation of 2. We have tried to minimize these effects by analysing our photolysed solutions immediately after photolysis, but some discrepancies may still have resulted.

Comparison of the results of the flash work reported here with steady state photolysis data must therefore concentrate on the early stages of photolysis where 2 comprises some 80%–85% of the photoproduct yield in aerated solution and is the only product detected in oxygen-saturated solution [8]. Both of these yields are rather larger than the values of 50% and 82% respectively which were calculated earlier. This discrepancy can be accounted for in a variety of ways. Firstly, we note that Grabner and coworkers [12,13] found the lifetime of 5 in the absence of oxygen to be of the order of 10 μs (i.e. $k_{1a} \approx 1.0 \times 10^5$ s^{-1}). This value was determined using a series of oxygen concentrations rather than the two values used here. A reduced k_{1a} rate constant means that a greater proportion of 5 reacts with molecular oxygen to yield 2. As above, with our lifetime values for 5 in aerated and oxygen-saturated solution, we find that 90% and 97% respectively of 5 will react with molecular oxygen. These percentages are now similar to the product yields of 2 during steady state photolysis and could therefore indicate that k_{1a} lies closer to 1.0×10^5 s^{-1} than 5.0×10^5 s^{-1}.

A second alternative is that some of the 5 which is produced does not react to yield photoproducts, but re-forms 4-CP. This would have the same effect on the predicted yields as reducing k_{1a}. Added chloride ions do not appear to affect the decay rate of either 5 or 6, but do reduce their yields, suggesting that they react with one of the earlier photochemical

intermediates (presumably the 4-hydroxyphenyl cation) to re-form 4-CP and thereby reduce the yields of the transient species derived from this earlier intermediate. However, 5 is sensitive to the proton concentration. Reaction with H^+ could yield the 4-hydroxyphenyl cation and thence 4-CP, thereby reducing the photoproduct yield from 5. The rate constant for this reaction is contained within the k_{1a} value, and would make it inappropriate to use our full k_{1a} value of $(5.4 \pm 1.0) \times 10^5$ s^{-1} when calculating the yields of 2 from the lifetimes of 5 under the various conditions.

Once formed, 6 reacts with water to produce 1,4-benzoquinone and hydrogen peroxide. The stoichiometry of the reaction is straightforward, but more than one mechanism could operate. The acceleration of the decay rate of 6 in the presence of H^+ suggests that the first step is protonation, and Grabner et al. [13] propose an ionic mechanism (Scheme 3(a)). However, it is not clear how the second step of this mechanism takes place. As an alternative, we propose the mechanism shown in Scheme 3(b), where oxygen plays a key role, but the second oxygen atom in 2 which is formed finally comes from a molecule of water.

In the absence of oxygen, the observed photoproducts are completely different and, in the absence of 6, the transient absorption is much weaker (Fig. 6). However, there is no reason to believe that the removal of oxygen interferes with the formation of 5, and the intensity of the first transient
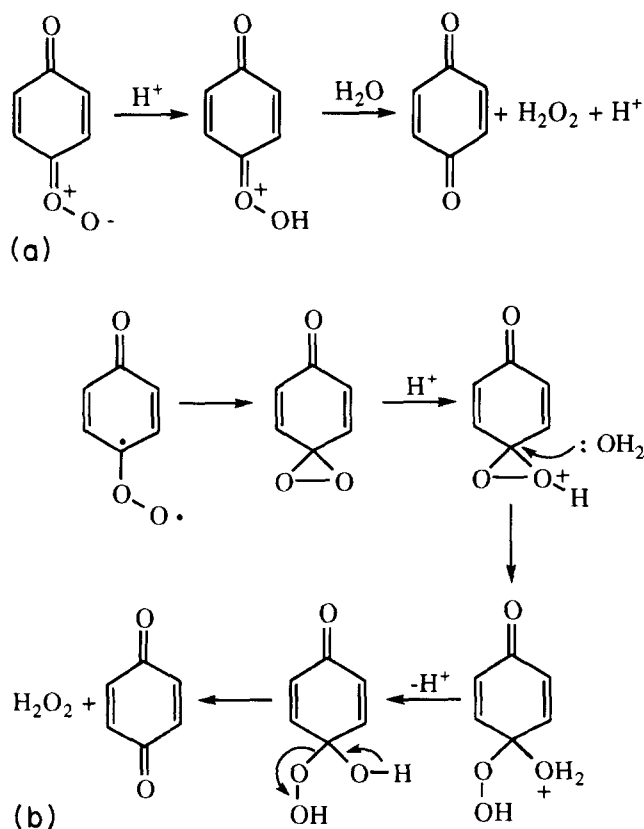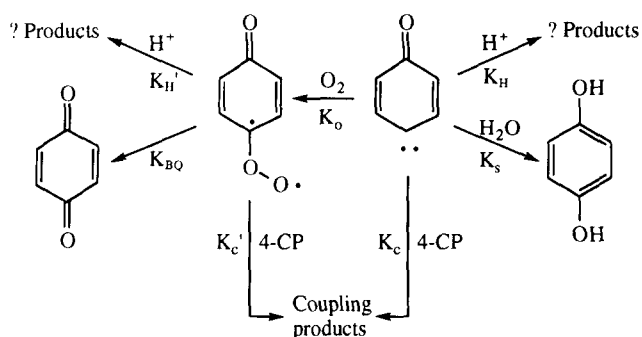
Scheme 4. Reactions of 5 in water.

Table 1
Comparison of the rate constants for the reactions of 5 and 6 from this work with those of Richard and Grabner [12]

Rate constant	This work	Ref. [12]	Units
k_O	$(1.9 \pm 0.4) \times 10^9$	3.5×10^9	dm^3 mol^{-1} s^{-1}
k_C	$(1.6 \pm 0.4) \times 10^8$	1.5×10^8	dm^3 mol^{-1} s^{-1}
$k_{C'}$	$(3.5 \pm 1.0) \times 10^7$	–	dm^3 mol^{-1} s^{-1}
k_S	$\approx 8.0 \times 10^2$	$\leqslant 1.5 \times 10^3$	dm^3 mol^{-1} s^{-1}
k_H	$(1.1 \pm 0.2) \times 10^9$	–	dm^3 mol^{-1} s^{-1}
$k_{H'}$	$(4.4 \pm 1.0) \times 10^8$	1.2×10^9	dm^3 mol^{-1} s^{-1}
k_{BQ}	$(9.0 \pm 2.0) \times 10^4$	8.0×10^4	s^{-1}

absorption spectrum is very similar in the 340–400 nm region for degassed and aerated solutions. We therefore conclude that the observed photoproducts in degassed solution also derive from 5. However, it is difficult to differentiate between the spectra of 5 and the long-lived transient which appears to be produced from it.

The photoproduct 3 in degassed or aerated solution can be viewed as arising from the insertion of the carbene into an O–H bond of water, although the actual mechanism may involve hydrogen abstraction to form a 4-hydroxyphenyl radical followed by radical recombination of this with the hydroxyl radical [13]. A similar hydrogen abstraction mechanism followed by dimerization would explain the formation of 2,2'- and 4,4'-dihydroxybiphenyl (and would predict the possible formation of 2,4'-dihydroxybiphenyl). Coupling products such as 2,4',5-trihydroxybiphenyl and 5-chloro-2,4'-dihydroxybiphenyl can arise via hydrogen abstraction from 3- and 4-CP respectively followed by radical recombination. The long-lived transient observed in degassed solution may be attributable to a combination of all the spectra of the above radicals.

The reactions of 5 following its formation are summarized in Scheme 4. The various rate constants for these reactions are given in Table 1 where they are compared (where available) with the results of Richard and Grabner [12].

In alkaline solution, there is evidence for the formation of both 5 and 6, albeit in reduced yield compared with neutral pH, together with a longer lived transient absorbing around 400 nm. The latter has been assigned by Grabner et al. [13] to the 4-chlorophenoxyl radical which is formed together with

Scheme 3. (a) Ionic mechanism for the formation of 1,4-benzoquinone (2) from 1,4-benzoquinone-O-oxide (6) [13]. (b) Possible mechanism for the formation of 1,4- benzoquinone (2) from 1,4-benzoquinone-O-oxide (6).

a hydrated electron. The kinetic behaviour of the transients has proved difficult to analyse, but it is clear that the decay of **6** is greatly accelerated at pH 12. This is presumably caused by attack of **6** by hydroxide ions to (eventually) yield 2-hydroxy-1,4-benzoquinone. The fate of the 4-chlorophenoxyl radicals is unclear at present and requires further work.

Acknowledgements

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