

Formation and Reactivity of 4-Oxocyclohexa-2,5-dienylidene in the Photolysis of 4-Chlorophenol in Aqueous Solution at Ambient Temperature

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Abstract: Nanosecond laser flash photolysis of an aqueous solution of 4-chlorophenol ($\lambda_{\text{exc}} = 266$ nm) produces, at pulse end, a transient with absorption maxima at 384, 370, and ca. 250 nm; upon addition of an H-donor such as 2-propanol, this spectrum is converted into that of the phenoxy radical ($\lambda_{\text{max}} = 400$ and 385 nm), and in presence of O_2 , it is converted into a transient with a broad absorption band peaking at 460 nm. This reaction behavior can be understood by assuming formation of the carbene, 4-oxocyclohexa-2,5-dienylidene, by elimination of HCl from excited 4-chlorophenol; the pulse end transient spectrum is assigned to this species, while the 460 nm band is assigned to benzoquinone *O*-oxide formed by addition of O_2 to the carbene. Both phenoxy radical and benzoquinone *O*-oxide are produced upon photolysis of 4-chlorophenol in neat alkanols as well. On the other hand, photolysis in *n*-hexane yields the triplet–triplet absorption, which is absent in polar solvents, and no indication of carbene formation. It can be concluded that the primary step of 4-chlorophenol photolysis in aqueous or alcoholic solution is heterolytic C–Cl bond scission; a quantum yield of 0.75 is determined for it in neutral or acid aqueous medium upon excitation at 266 nm. Photolysis of chlorophenolate produces the same transients, but with a markedly lower yield, and, in addition, e_{aq}^- and 4-chlorophenoxy radicals. The proposed reaction mechanism provides a straightforward explanation of the results of photoproduct analysis, published by previous authors as well as contributed in the present work. In particular, formation of *p*-benzoquinone in the presence of O_2 can be accounted for by intermediate formation of benzoquinone *O*-oxide. Production of 4-oxocyclohexa-2,5-dienylidene with high yield allows, for the first time, extensive investigation of the kinetics and mechanism of the reactions of a carbene in an aqueous environment. In the present work, we have studied (a) the addition reaction with O_2 on the one hand and with halides on the other; (b) H abstraction reactions with alkanols; (c) reaction with 4-chlorophenol itself; and (d) reaction with H_2O . The rate constants for reaction with O_2 ($3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and with I^- ($4.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are close to the diffusion-controlled limit, whereas reactions with Br^- ($6.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and Cl^- ($< 3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) are slower. Rate constants for reaction with alkanols follow the pattern known for their reactions with radicals, with values ranging from $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for *tert*-butyl alcohol to $1.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 2-butanol. All these observations are consistent with the triplet character of the carbene. A rate constant of $1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ has been determined for reaction with H_2O . This reaction is not accompanied by formation of OH radicals; it is concluded that it proceeds by insertion into the O–H bond rather than by O–H cleavage. The exceptional stability of the carbene in aqueous solution is thus mainly attributed to the high barrier for O–H rupture in the water molecule. Additionally, a specific carbene– H_2O interaction is revealed by semiempirical calculations, which could contribute to energetic and orientational hindrance of the reaction. Further theoretical results support the interpretation of both spectroscopic and kinetic properties of the carbene.

Introduction

The solution photochemistry of the aromatic carbon–halogen bond is a subject of long-standing interest.¹ Homolytic carbon–halogen cleavage upon photoexcitation of aryl halides has been known for a long time² and exploited for synthetic purposes. The efficiency of this process is expected, and experimentally found, to depend on the strength of the C–X bond, resulting in scant photochemical activity of F- or Cl-substituted compounds. On the other hand, nucleophilic photosubstitution reactions on

substituted aryl halides have been studied extensively by Havinga and his group.³ For instance, photocyanation, -methoxylation, or -hydroxylation of halogenoanisoles occur with high yield in *tert*-butyl alcohol/water solution upon excitation in their lowest (S_1) absorption band.⁴ This process was thought to involve photoionization of the triplet excited aryl halide, followed by reaction of the radical cation with the nucleophile.⁴ Other authors, however, reached different mechanistic conclusions concerning nucleophilic photosubstitution, for example formation of a σ (Meisenheimer) complex between the excited molecule and the nucleophile⁵ has been suggested, as well as initial electron transfer to the aryl halide, yielding a radical anion.⁶

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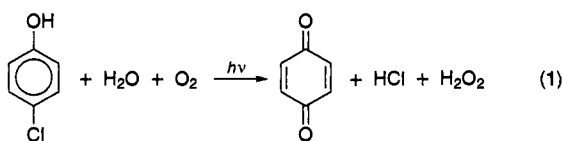
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Despite these disagreements, one general conclusion of these studies was that nucleophilic photosubstitution requires a heterolytic dissociative step at some stage of the mechanism. The process is enhanced by activating substituents such as methoxy,⁴ but it is not limited to substituted compounds; for instance, photolysis of chlorobenzene in ethanol/water at $\lambda_{exc} = 254 \text{ nm}$ ⁷ yielded phenol and phenetole as products along with HCl and benzene, indicating competition of nucleophilic substitution with homolysis, although the quantum yields of the former did not exceed 0.1. The lack of an oxygen effect on this yield let the authors conclude that a singlet pathway was operative in photosubstitution, with either a radical cation or a carbocation as the reactive intermediate. This latter possibility was also envisaged in a study of the photohydrolysis of 3,4-dichloroaniline.⁸ Competition between homolytic and heterolytic dissociation pathways is also observed in the photochemistry of alkyl halides.⁹

These earlier efforts thus were unable to clarify the mechanism of nucleophilic photosubstitution of aryl halides. One problem consisted of the fact that mechanisms were inferred from product studies without recourse to time-resolved techniques. One notable exception was a detailed study of 4-fluoro- and 4-chloroanisole in acetonitrile/water and *tert*-butyl alcohol/water by nanosecond transient absorption spectroscopy;¹⁰ according to this study, photosubstitution proceeds by ionic dissociation of a triplet exciplex in the presence of water and subsequent reaction of the radical cation with the nucleophile. The previously postulated⁴ formation of radical cations by electron photoejection from excited triplet molecules was ruled out on the basis of the time-resolved study.

Interest in the photochemistry of aryl halides has regained strength in recent years in the course of the research effort aimed at developing techniques for photodegradation of organic pollutants; in this respect, halogenated phenols have been among the most studied substrates. Knowledge of product distributions upon photolysis in aqueous solutions has accumulated, thanks in particular to the efforts of Boule and co-workers.¹¹ More recently, a further research line has been opened by Lipczynska-Kochany and co-workers, who applied a combination of pulsed excitation and product analysis (HPLC) to the study of the photolysis of 4-chlorophenol¹² and 4-bromophenol.¹³ One of the remarkable results of these studies is the fact that *p*-benzoquinone is formed as the main product of 4-chlorophenol photolysis in neutral aqueous solution in the presence of oxygen; this process requires one photon and no precursor can be detected in product studies. This finding implies a fast reaction sequence according to the overall stoichiometry:



In deoxygenated aqueous solution, phototransformation of 4-chlorophenol yields several products; the major ones are

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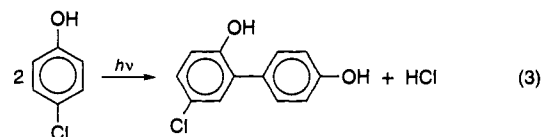
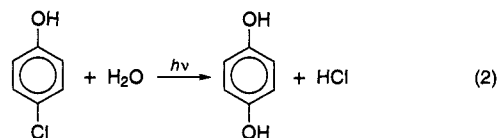
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hydroquinone and 5-chloro-2,4'-dihydroxybiphenyl,^{14,15} corresponding to the stoichiometries



4,4'-Dihydroxybiphenyl, 2,5,4'-trihydroxybiphenyl, and oligomers with three or four phenolic rings have been detected as minor products.¹⁶

Reports about detection of *p*-benzoquinone in deoxygenated solution are contradictory. According to Oudjehani and Boule,¹⁶ no *p*-benzoquinone is found in this case; other authors find either a somewhat reduced yield in argon-saturated solution¹² or no effect of deoxygenation.¹⁷

Elimination of HCl is thus involved in each of the three main photolytic reaction paths; the participation of H₂O in the overall stoichiometry of reactions 1 and 2 furnishes a first indication that a heterolytic (photohydrolytic) mechanism is at work. It is not known, however, which individual steps might be involved, and as far as *p*-benzoquinone formation is concerned not even a plausible proposal has been formulated so far.

We have now undertaken to examine the details of the photolysis mechanism of 4-chlorophenol upon excitation in its first singlet absorption band by means of nanosecond transient absorption spectroscopy. This study is focused upon aqueous solutions; measurements performed in other solvents are included to lend support to the proposed mechanism. With the same goal, chemical analysis of photolysis products has been carried out wherever literature data seemed insufficient.

Results

1. Transient Absorption Experiments. (a) **Neutral Deoxygenated Aqueous Solutions.** Photolysis of argon-saturated aqueous 4-chlorophenol at pH values around 6 results in a transient spectrum exhibiting, at pulse end, a two-band absorption with $\lambda_{max} = 370$ and 384 nm and an additional band in the far-UV, with $\lambda_{max} = 250$ nm (Figure 1).

An additional weak band is present at longer wavelengths ($\lambda_{max} \approx 580$ nm). At longer times, the transient spectrum is transformed into a broad unstructured band with $\lambda_{max} = 395$ nm. The insert in Figure 1 shows the time course of the absorbances at 250, 384, and 400 nm; at the latter wavelength, the formation kinetics of the secondary product is seen, and this buildup is mirrored by the decay at 250 nm. At the absorption maximum of the primary transient, the absorbance changes only little with time due to overlap with the formation of the secondary transient. The absorption of the latter partly decays within 100 μs , but a larger fraction is long-lived with a half-life of about 50 ms. Pulse energy dependence shows linearity with photon fluence in the low fluence range for all these species; more generally, this was found to be true for all transients detected from 4-chlorophenol photolysis, with the exception of e_{aq}^- and the corresponding radical (see below). A

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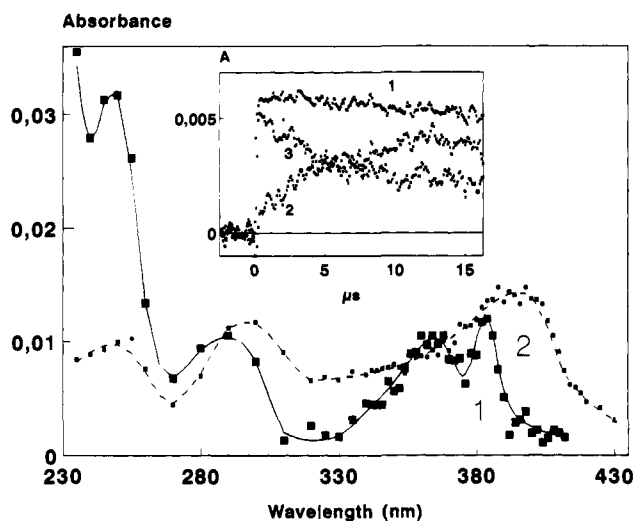


Figure 1. Uncorrected transient spectra from 1.2×10^{-3} M 4-chlorophenol in neutral argon-saturated solution at 0.3 mJ/pulse: (1) pulse end; (2) 16 μ s after pulse end. *Insert:* Time course of absorbance (0.1 mJ/pulse) at 384 nm (1); absorbance multiplied by a factor of 1.5, 400 nm (2) and 250 nm (3); absorbance multiplied by a factor of 0.5).

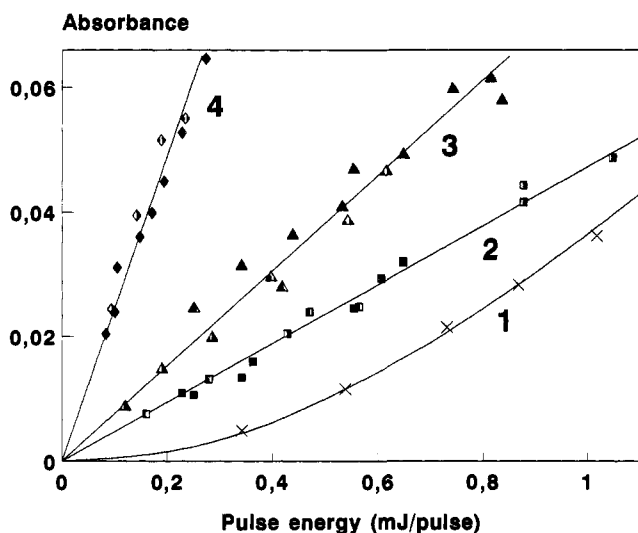


Figure 2. Dependence of transient absorbances from neutral aqueous 4-chlorophenol solutions on pulse energy (all data normalized to a ground-state absorbance of 1 at 266 nm): (1) argon-saturated solution, pulse end, $\lambda = 720$ nm; (2) argon-saturated solution, pulse end, $\lambda = 384$ nm; (3) argon-saturated solution containing ethanol (0.33–1.26 M), 1–5 μ s after pulse end, $\lambda = 400$ nm; (4) O_2 -saturated solution, 1 μ s after pulse end, $\lambda = 460$ nm.

selection of pulse energy dependences of end-of-pulse absorbances is shown in Figure 2. One-photon mechanisms of transient formation are indicated in all linear cases.

(b) Influence of Oxygen. Irradiation of a neutral aqueous solution of 4-chlorophenol in the presence of O_2 produces a pulse-end spectrum similar to that of Figure 1, but the secondary spectrum now is a broad band with $\lambda_{\max} = 460$ nm, shown in Figure 3. As shown in Figure 4, the first-order formation rate constant at 460 nm was found to be proportional to the oxygen concentration, corresponding to a reaction of the 384/370 nm species with O_2 with a rate constant of $3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The 460 nm band decayed in a first-order reaction with a rate constant of $5.5 \times 10^4 \text{ s}^{-1}$ at neutral pH. This decay was accelerated at higher pulse energies; at 1 mJ/pulse, the rate constant was $1.05 \times 10^5 \text{ s}^{-1}$.

(c) Influence of 4-Chlorophenol Concentration. The transient spectra in deoxygenated aqueous solution were found to be independent of the concentration of 4-chlorophenol, but

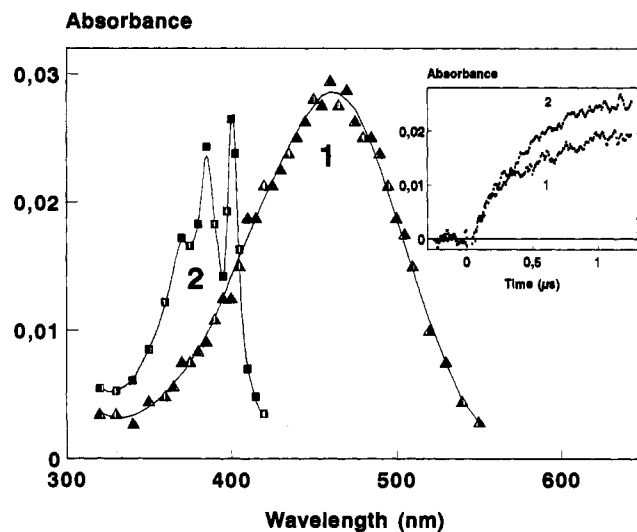


Figure 3. Transient spectra, measured 1 μ s after pulse end from 1.5×10^{-3} M 4-chlorophenol in neutral aqueous solution: (1) solution saturated with O_2 , 0.25 mJ/pulse, absorbances multiplied by a factor of 0.5; (2) argon-saturated solution, 0.26 M 2-propanol added, 0.35 mJ/pulse. *Insert:* Time course of absorbance: (1) 1.5×10^{-3} M 4-chlorophenol + 0.13 M 2-propanol, 0.32 mJ/pulse, $\lambda = 400$ nm; (2) 5×10^{-4} M 4-chlorophenol + 2.65×10^{-4} M O_2 , $\lambda = 460$ nm.

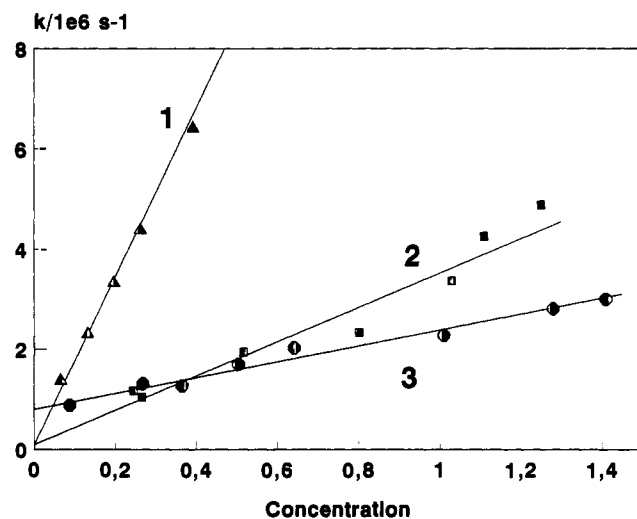


Figure 4. Transient kinetics as a function of reactant concentration in pulse-irradiated neutral aqueous 4-chlorophenol solutions: (1) formation rate constant at 400 nm vs concentration of added 2-propanol (in M); (2) formation rate constant at 460 nm vs concentration of O_2 (in mM); (3) decay rate constant at 250 nm (multiplied by a factor of 10) vs concentration of 4-chlorophenol (in mM).

the buildup kinetics around 400 nm as well as the decay of the primary absorption in the far-UV (250 nm) became faster when the concentration was raised, hinting at a reaction of a primary transient with the substrate. The first-order decay at 250 nm was proportional to the concentration of 4-chlorophenol (Figure 4), the resulting second-order rate constant being $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This effect was confirmed by studying the influence of 4-chlorophenol concentration on the 460 nm transient in a solution containing 2.65×10^{-4} M O_2 , which was found to decrease with increasing concentration. The data of Figure 4 further yield a limiting first-order rate constant of $8 \times 10^4 \text{ s}^{-1}$ for the decay at 250 nm at zero 4-chlorophenol concentration.

(d) Influence of Addition of Alkanols. The same end-of-pulse transient spectrum was again obtained upon irradiation of a deoxygenated neutral aqueous solution of 4-chlorophenol containing 2-propanol. The 384/370 species now transformed into a two-band secondary transient with $\lambda_{\max} = 385$ and 400

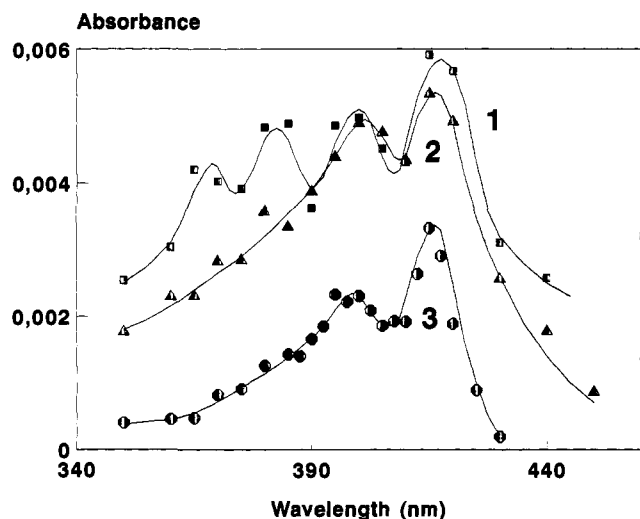


Figure 5. Transient spectra from 5.6×10^{-4} M 4-chlorophenol, pH 12.3, saturated with argon (0.4 mJ/pulse): (1) pulse end; (2) $8 \mu\text{s}$ after pulse end. (3) Spectrum of 4-chlorophenoxyl radical measured $2 \mu\text{s}$ after pulse end (0.19 mJ/pulse) in a neutral solution of 3.6×10^{-4} M 4-chlorophenol + 0.2 M $\text{S}_2\text{O}_8^{2-}$.

nm (Figure 3). The first-order formation rate constant was proportional to the concentration of the alcohol (Figure 4). This species decayed in a second-order reaction with $2k/\epsilon = 7.7 \times 10^5 \text{ cm s}^{-1}$. Based on the location of the band maxima and on the decay kinetics, it can be assigned to the unsubstituted phenoxyl radical;¹⁸ this assignment is well-founded since 4-chlorophenoxyl radicals, which could alternatively be formed upon photolysis, absorb at distinctly longer wavelengths (see below). If oxygen is present, both the 400/385 and the 460 nm transients are formed, the ratio of absorbances indicating competition for the same precursor; the absorbance at 460 nm is proportional to $[\text{O}_2]$ in a solution containing 2-propanol. The decay of the 460 nm species was not affected by addition of an alcohol.

(e) Photochemical Formation of Hydrated Electrons. At higher pulse energies, the characteristic absorption band of e_{aq}^- could be measured at pulse end; it was found to decay in a pseudo-first-order reaction with 4-chlorophenol ($k = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). At low pulse energies, the e_{aq}^- absorbance increased in a markedly nonlinear (quadratic) manner, indicating a two-photon formation mechanism (Figure 2). The production of 4-chlorophenoxyl radicals is expected along with that of e_{aq}^- . Since the extinction coefficient of this radical at its band maximum (415 nm) is less than one fifth of that of e_{aq}^- at 720 nm (see below), contributions arising from photoionization can be neglected at the pulse energies used to investigate the other 4-chlorophenol transients ($P < 0.5$ mJ/pulse).

(f) Transients in Alkaline Solutions. Photolysis of 4-chlorophenolate ($\text{p}K_{\text{a}} = 9.4^{19}$) again generates e_{aq}^- , this time in a one-photon process with $\Phi = 0.095$. This behavior is analogous to that of phenol and other substituted phenols,²⁰ and the quantum yield is of the same order of magnitude. The e_{aq}^- decayed by reaction with 4-chlorophenolate with a rate constant of $6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Further transients obtained in alkaline solution feature peaks at 370, 384, 400, and 415 nm (Figure 5). A new species is thus formed in alkaline medium together with the 384/370 nm transient; it can be assigned to the 4-chlorophe-

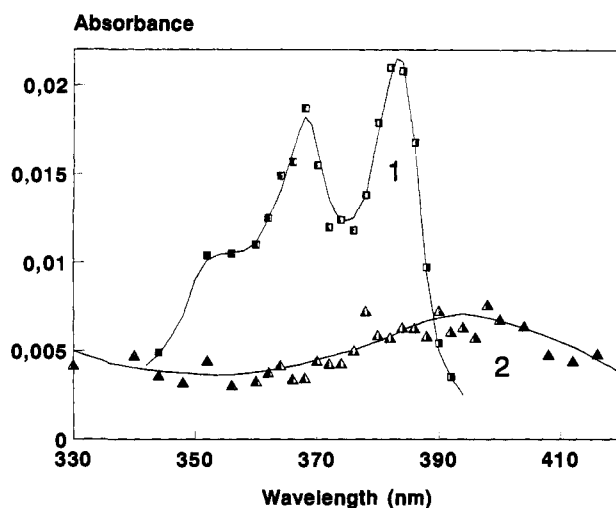


Figure 6. Transient spectra from 2.2×10^{-3} M 4-chlorophenol, pH 0.7, saturated with O_2 (0.38 mJ/pulse): (1) pulse end; (2) $1.6 \mu\text{s}$ after pulse end.

noxyl radical formed together with e_{aq}^- . This assignment is confirmed by its production via one-electron oxidation by sulfate radicals following photolysis of peroxodisulfate in the presence of 4-chlorophenol; the resulting radical exhibits the same 415/400 nm band structure (Figure 5). Two one-photon processes thus occur simultaneously in the photolysis of 4-chlorophenolate. This is corroborated by the observation that O_2 and 2-propanol act in the same way as in neutral solution, producing the 460 and 400/385 nm transients, but the transient yields (including that of the 384/370 nm one) are of the order of 10% only of their values in neutral solution.

(g) Behaviour in Acid Solutions. Transient absorptions in argon-saturated solutions, both in the absence and in the presence of 2-propanol, are much the same in the pH range between 0 and 7. The only effect of decreased pH is an acceleration of the decay of the 460 nm transient formed in the presence of O_2 ; a rate constant of $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is determined for reaction of this transient with H^+ . As a consequence, the decay of the 460 nm transient becomes faster than its formation in strongly acid solution, and its absorption is correspondingly reduced. The spectrum of the 384/370 nm transient is therefore most accurately measured in this condition; the result is shown in Figure 6.

(h) Nonaqueous Solvents. Transient spectra were measured in a range of solvents, including alkanols, acetonitrile, and *n*-hexane; the results demonstrate that 4-chlorophenol photochemistry is strongly solvent dependent. Transient absorptions in alkanol solutions (Figure 7) are reminiscent of those in aqueous solutions; only the 400/385 nm species is obtained in argon-saturated solution, but the 460 nm band is additionally present when the solutions are saturated with O_2 (albeit somewhat red-shifted, especially in 2-propanol).

The amount of the 400/385 nm absorption relative to the 460 nm absorption increases in the sequence methanol < ethanol < 2-propanol; this corresponds to the trend observed in the rate constants of the 384/370 nm transient with the same alcohols in aqueous solution (see Table 2 below). It is therefore probable that this transient is also formed in the alcohols, its lifetime being too short to be accessible at our time resolution, and this means that the photolysis mechanism is likely to be the same as in water. Transients obtained in acetonitrile and *n*-hexane are, however, markedly different; in the former solvent, only two-photon formation of 4-chlorophenoxyl radicals is seen; in the presence of O_2 , a weak band with $\lambda_{\text{max}} = 490$ nm is additionally observed. In *n*-hexane, on the other hand, photolysis in deoxygenated solution produces a strong transient with

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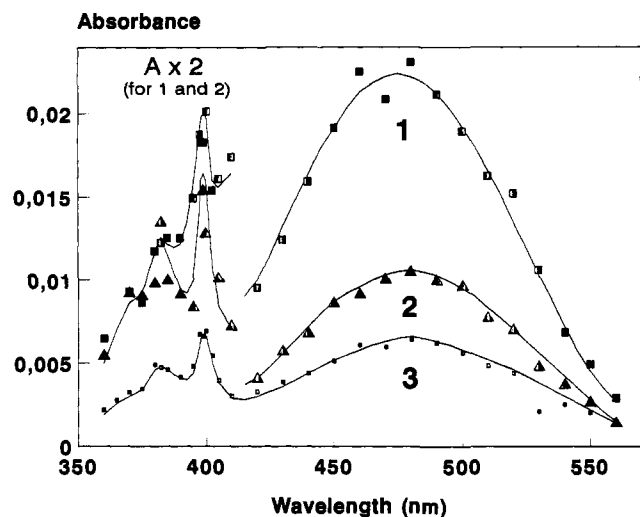


Figure 7. Transient spectra from 5.2×10^{-4} M 4-chlorophenol in alkanols, saturated with O_2 , measured at pulse end (0.5 mJ/pulse): (1) methanol; (2) ethanol; (3) 2-propanol.

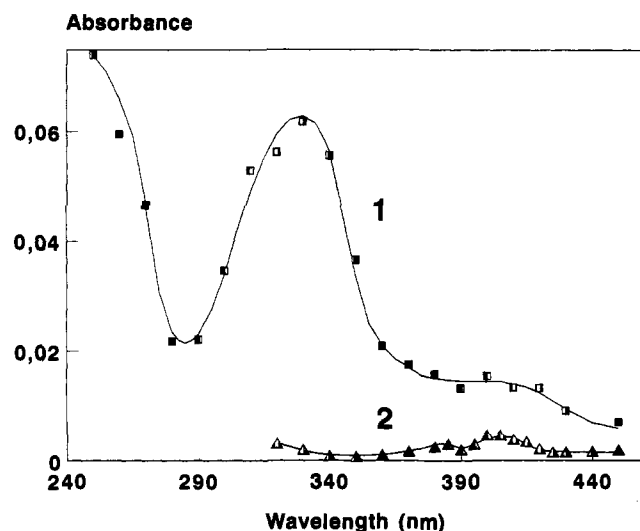


Figure 8. Uncorrected transient spectra from 7.5×10^{-4} M 4-chlorophenol in *n*-hexane, measured at pulse end (1.2 mJ/pulse): (1) solution saturated with argon; (2) solution saturated with O_2 .

$\lambda_{\max} = 330$ nm (Figure 8), reminiscent of the triplet-triplet absorption of chlorobenzenes.²¹

In agreement with this assignment, the 330 nm band is quenched by O_2 . A weak transient remains with $\lambda_{\max} \approx 400$ and 385 nm; although these band maxima are consistent with those of the phenoxyl radical, the absorption is too broad in order to be assigned due to this species alone.

(i) Photophysical Properties. In neutral aqueous solution, 4-chlorophenol fluoresces very weakly, with $\tau_F \approx 500$ ps. No fluorescence can be detected in alkaline medium. Attempts to locate a triplet-triplet absorption by means of the effect of the triplet quencher acrylamide were unsuccessful; the transient spectrum was unaltered upon its addition. Energy transfer to anthracene ($\lambda_{exc} = 280$ nm) was used to estimate formation of 4-chlorophenol triplet states in ethanol and *n*-hexane; the quantum yield of anthracene triplets populated by energy transfer was found to be close to 1 in *n*-hexane, but below the detection limit ($\Phi < 0.005$) in ethanol. This result further strengthens the assignment of the 330 nm band, which among the solvents examined was only found in *n*-hexane, to the triplet-triplet absorption of 4-chlorophenol; and it shows that in ethanol the lowest triplet state of 4-chlorophenol is either not populated or has a very short lifetime. Based on $\Phi = 1$, an extinction

Table 1. Quantum Yields of Primary Photoproducts from Neutral Aqueous 4-Chlorophenol (7×10^{-4} M) Irradiated at 280 nm

product	condition	quantum yield
4-chlorophenol ^a	O_2 saturated	0.64
Cl^-		0.68
H^+		0.70
<i>p</i> -benzoquinone		0.58
H_2O_2		0.60
hydroquinone		0.01
5-chloro-2,4'-dihydroxybiphenyl		0.01
4-chlorophenol ^a	argon saturated	0.83
hydroquinone		0.20
5-chloro-2,4'-dihydroxybiphenyl		0.16
4,4'-dihydroxybiphenyl		≈ 0.01
4-chlorophenol ^a	argon saturated	0.68
phenol	1.2 M methanol	0.48
hydroquinone		0.01
4-methoxyphenol		0.009
4,4'-dihydroxybiphenyl		0.013
2,2'-dihydroxybiphenyl		0.013
4-bromophenol	argon saturated, 0.011 M Br^-	0.58

^a Quantum yield of 4-chlorophenol disappearance.

coefficient $\epsilon_{330} = 8500 \text{ M}^{-1} \text{ cm}^{-1}$ is determined for the triplet-triplet transition in *n*-hexane.

(j) Photolysis of 3-Chlorophenol. Only very weak ($A < 0.001$) transient absorptions could be detected in a neutral aqueous solution of 3-chlorophenol upon excitation at 266 nm with pulse energies comparable to those used for studying the 4-isomer. At higher pulse energies, a two-band transient ($\lambda_{\max} = 415$ and 430 nm) appeared together with the absorption of the hydrated electron; both absorptions increased linearly with the square of the pulse energy. This behavior is characteristic for a two-photon ionization process, and the 430/415 nm bands are therefore assigned to the 3-chlorophenoxyl radical. One-photon transformation of 3-chlorophenol is thus not experimentally accessible in the transient absorption spectrum.

2. Product Analysis. Analysis of products formed upon irradiation of aqueous 4-chlorophenol with low intensities ($\lambda_{exc} = 280$ nm) was carried out in order to complement the data gained by transient absorption spectroscopy. The quantum yields of primary products (as opposed to secondary products involving photolysis of primary products) measured in moderately concentrated solutions ($\approx 7 \times 10^{-4}$ M) in different conditions are summarized in Table 1.

HPLC analysis of neutral solutions confirms that hydroquinone and 5-chloro-2,4'-dihydroxybiphenyl are formed in deoxygenated solutions, whereas no *p*-benzoquinone can be detected.¹⁶ In the presence of oxygen, *p*-benzoquinone is the main primary product, in agreement with the observations made by several authors.^{12, 16, 17} Careful analysis of the dependence of the yield of another known product, 2,5,4'-trihydroxybiphenyl,¹⁶ on irradiation dose showed that this is not a primary product.

Additional products detected in all cases were H^+ , as evidenced by the pH decrease of the irradiated solution, and Cl^- ions. In the presence of O_2 , H_2O_2 was formed with a yield equalling that of *p*-benzoquinone; this was also true in solutions containing 2-propanol, in which case both products were equally quenched. The Cl^- and H^+ yields were not affected by addition of O_2 or of 2-propanol. At low absorbed doses, the yields of H^+ , Cl^- , and H_2O_2 were found to be equal to that of 4-chlorophenol disappearance within $\pm 10\%$. Table 1 shows that these yields are quite high, with an average value of $\Phi = 0.63$ in presence of O_2 .

Previous results obtained at two distinct 4-chlorophenol concentrations¹⁶ had indicated that product yields are concentration dependent. We have now measured the quantum yields of 4-chlorophenol disappearance as well as those of hydro-

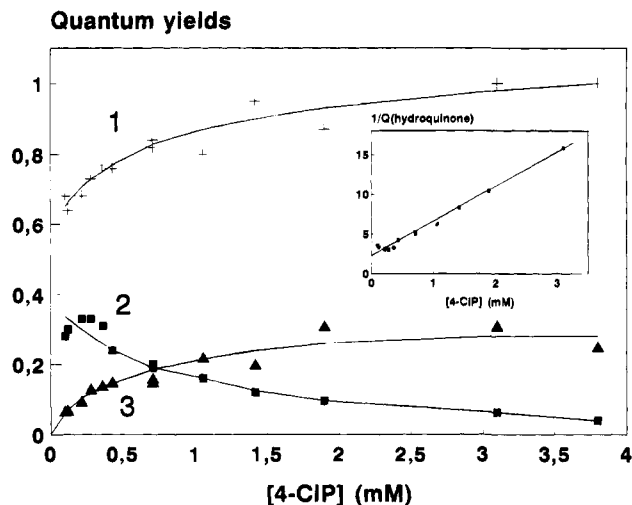


Figure 9. Influence of 4-chlorophenol concentration on the quantum yields of 4-chlorophenol disappearance (1) and of formation of hydroquinone (2) and of 5-chloro-2,4'-dihydroxybiphenyl (3) in neutral argon-saturated solution upon excitation at 280 nm. *Insert:* Dependence of the inverse of the hydroquinone quantum yield on 4-chlorophenol concentration.

quinone and 5-chloro-2,4'-dihydroxybiphenyl formation in deoxygenated solutions at various 4-chlorophenol concentrations ranging from 10^{-4} to 3.8×10^{-3} M. The results are presented in Figure 9.

The data demonstrate that the two photoproducts exhibit opposed concentration dependences, the yield of hydroquinone decreasing and that of the dimer increasing with increasing 4-chlorophenol concentration. The disappearance quantum yield increases from about 0.65 to about 1 in the concentration range studied. According to reactions 2 and 3, the disappearance quantum yield should equal the sum of the quantum yield of hydroquinone formation plus twice the quantum yield of dimer formation. The data do not fully conform to this expectation, indicating that further photoproducts are missed by the HPLC analysis. In contrast, the disappearance quantum yield does not depend on 4-chlorophenol concentration in an oxygenated solution, where it equals 0.65.

In the insert of Figure 9, the quantum yields of hydroquinone formation obtained in the absence of oxygen solution are replotted assuming a competing reaction of a precursor with 4-chlorophenol. Good linearity is obtained in confirmation of this assumption and a limiting quantum yield of 0.44 can be deduced for hydroquinone formation at low 4-chlorophenol concentrations. The limiting quantum yield of 4-chlorophenol disappearance cannot be determined with certainty from Figure 9, but it appears to be around 0.6; this is still somewhat higher than the quantum yield of hydroquinone formation, but the discrepancy is somewhat less pronounced than at higher concentrations, indicating that the majority of products missed in the HPLC analysis arise from reactions of a photoproduct species with 4-chlorophenol.

Upon addition of an alkanol, the yields of all products mentioned above decreased and phenol appeared as a new major product; the disappearance quantum yield was independent on the alkanol concentration. This is shown in Figure 10 along with the opposing trends in benzoquinone and phenol quantum yields in an oxygenated solution at various concentrations of 2-propanol. The sum of both is lower than the disappearance quantum yield by no more than 10%.

Some minor products were identified along with phenol in a deoxygenated solution containing methanol, the quantum yields of each being <0.02 (Table 1)—4-methoxyphenol and the three isomeric dihydroxybiphenyls—among these, at least 4,4'-dihy-

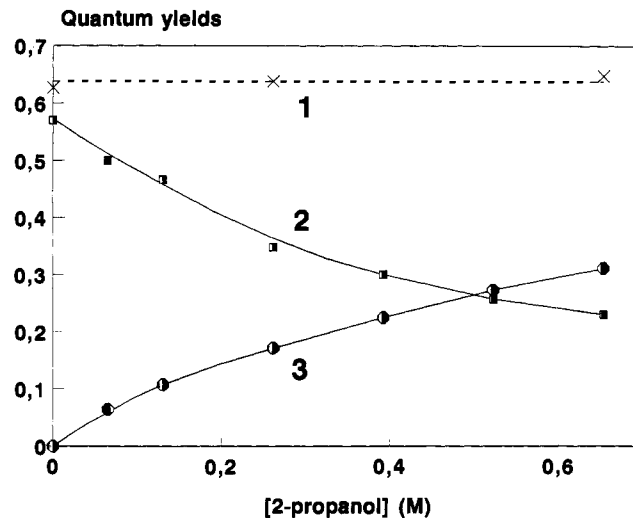


Figure 10. Influence of the concentration of 2-propanol on the quantum yields of 4-chlorophenol disappearance (1) and of formation of *p*-benzoquinone (2) and of phenol (3) in neutral, O_2 -saturated solutions of 4-chlorophenol (7.1×10^{-4} M) excited at 280 nm.

droxybiphenyl is also formed in solutions which do not contain an alcohol, as it was always present in small amounts among the products.

Photolysis of 4-chlorophenolate in alkaline solution gave basically the same product distribution as did irradiation of undissociated 4-chlorophenol, but quantum yields were smaller; the Cl^- quantum yield was found to be 0.22 at pH 11.2.

The effect of addition of Br^- on 4-chlorophenol photolysis was also studied. In this case, 4-bromophenol appears as a new product; at 0.01 M Br^- , its formation is quantitative and no other products are detected by HPLC. When 4-bromophenol is irradiated in the presence of Br^- , no photoreaction is observed, whereas otherwise its photoproduct distribution is very similar to that of 4-chlorophenol. Addition of Cl^- to a solution of 4-bromophenol does not, however, yield 4-chlorophenol unless very high concentrations (>0.4 M) are used. The same applies to solutions of 4-fluorophenol.

Finally, a search for photoproducts was made in those non-aqueous solvents where the 384/370 nm transient could not be observed. The HPLC analysis of products from photolysis of 4-chlorophenol in acetonitrile as well as in *n*-hexane yielded phenol, with a very low quantum yield ($\Phi \approx 0.002$) in acetonitrile and with a more sizable one ($\Phi = 0.08$) in *n*-hexane. In the latter solvent, two minor non-identified products were also detected.

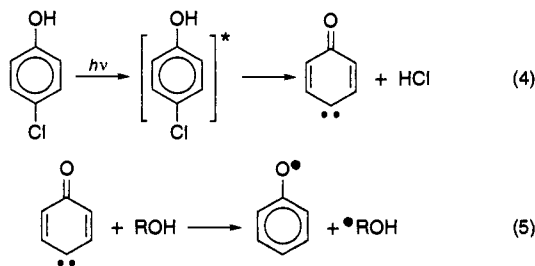
Discussion

1. Mechanism of Primary Photoreactions. Among the absorbing transients resulting from pulsed irradiation of 4-chlorophenol in a number of solvents, several allowed easy assignment as shown above; these included the following: (a) the phenoxyl radical formed in the presence of alkanols, and probably in neat *n*-hexane; (b) the 4-chlorophenoxyl radical arising from photoionization (two-photon in neutral aqueous solution and in acetonitrile, one-photon in alkaline aqueous solution); and (c) the triplet-triplet absorption which could only be detected in the nonpolar solvent *n*-hexane.

The transients remaining to be identified are the 384/370 nm two-band transient appearing as a primary product (at 50 ns time resolution) in aqueous solution (Figure 1) and the 460 nm transient resulting from its reaction with O_2 (Figure 3). Both species are also observed in solutions of 4-chlorophenol in alkanols, but not in acetonitrile and *n*-hexane.

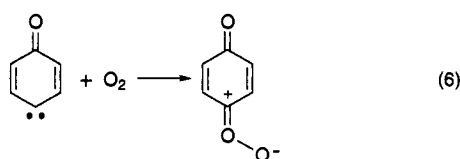
The spectrum of the 384/370 nm species is reminiscent of a phenoxyl-type radical but distinct from any known radical of

this family,^{18b} all of which absorb at somewhat longer wavelengths. Its assignment is aided by its characteristic reactivity with alkanols which can be assumed to act as H donors; the observation of the formation of an unsubstituted phenoxy radical by addition of an H atom can be accounted for by the following reaction sequence:



Based on this reaction sequence, the 384/370 nm absorption is assigned to 4-oxocyclohexa-2,5-dienylidene (called "carbene" in the following). This assignment is supported by related observations reported in recent literature: this carbene has been generated at cryogenic temperatures by photolysis of the corresponding quinone diazide (4-diazo-2,5-cyclohexadienone) and characterized by matrix isolation spectroscopy.²² Its absorption spectrum shows the same two-band structure in the 370–390 nm region as the primary transient found in our study. On the other hand, in a recent study of nanosecond laser flash photolysis of the quinone diazide in 1,1,2-trichlorotrifluoroethane (Freon-113),²³ the carbene could be indirectly detected via its reactions with triplet oxygen, cyclohexane, methanol, and ylide-forming reactants; however, its direct identification by transient absorption spectroscopy was prevented by bleaching of the diazo precursor. Following reaction with cyclohexane, the absorption of the phenoxy radical could be detected, and this was explained by an H-abstraction reaction analogous to reaction 5.

According to ESR measurements,²⁴ the ground state of the carbene is a triplet, and it should therefore be reactive toward oxygen. Indeed, its reaction with O₂ has been shown by matrix isolation spectroscopy²⁵ as well as by transient absorption experiments²³ to form *p*-benzoquinone *O*-oxide:



This species is characterized by a strong absorption band, centered around 460 nm, which is very similar to that found in O₂-saturated solutions of 4-CIP (Figure 3).

Assignment of the 384/370 nm species to the carbene is thus based on similarity of its absorption spectrum to that measured in matrix isolation conditions and, perhaps more significantly, on identification of the products of its reactions with an H-donor on the one hand and with O₂ on the other. It has to be added, however, that attempts to detect transients arising from eventual reactions with ylide-forming reactants such as acetonitrile and acetone were unsuccessful, in contrast to what has been observed

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(24) (a) Wasserman, E.; Murray, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 4203. (b) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *113*, 5311.

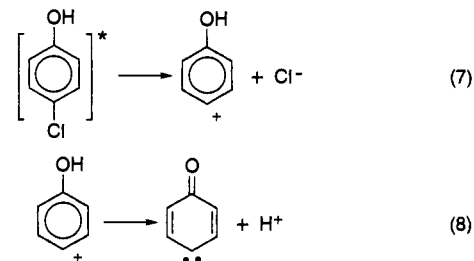
(25) Sander, W. *J. Org. Chem.* **1988**, *53*, 2091.

in a nonpolar solvent;²³ pyridine could not be used as a trapping agent because its ground-state absorption overlaps that of 4-chlorophenol. Some formation of phenoxy radicals was found at high concentrations of acetonitrile (>1 M) in aqueous solution, but not in neat acetonitrile.

Assuming complete conversion into phenoxy radicals by reaction with 2-propanol (reaction 5), the quantum yield of carbene formation can be determined based on the known extinction coefficient of the phenoxy radical ($\epsilon_{400} = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ ^{18a}); in neutral or acid aqueous solution, the result is $\Phi = 0.75$ at $\lambda_{\text{exc}} = 266 \text{ nm}$ and $\Phi = 0.70$ at $\lambda_{\text{exc}} = 280 \text{ nm}$, and $\Phi = 0.63$ at $\lambda_{\text{exc}} = 266 \text{ nm}$ in alkanols (identical within error limits for methanol, ethanol, and 2-propanol). From the laser pulse energy dependence of the carbene yield (Figure 2), an extinction coefficient of $2000 \text{ M}^{-1} \text{ cm}^{-1}$ is deduced at $\lambda = 384 \text{ nm}$; the extinction coefficient of the weak long-wavelength band is $\epsilon_{580} \approx 100 \text{ M}^{-1} \text{ cm}^{-1}$. Using the same method, the extinction coefficient of benzoquinone *O*-oxide at 460 nm is found to be $9500 \text{ M}^{-1} \text{ cm}^{-1}$. In view of the experimental uncertainties of actinometry and transient absorption measurement, the quantum yields determined upon excitation at 280 nm for 4-chlorophenol disappearance on the one hand and for carbene formation on the other, using respectively pulsed and steady-state excitation, can be considered to be in good agreement.

There is at present no direct experimental evidence concerning the mechanism of HCl elimination from excited chlorophenol. The carbene is produced with high quantum yield, indicating that all steps involved in its formation are fast in comparison with competing steps such as nonradiative deactivation or other photochemical pathways. HCl elimination appears to require a polar protic environment as it takes place neither in *n*-hexane nor in acetonitrile. In *n*-hexane, phenol is produced with a moderate quantum yield ($\Phi = 0.08$), but obviously not *via* the carbene route since no benzoquinone *O*-oxide is found in a solution saturated with O₂ (Figure 8). No significant one-photon photochemistry takes place in acetonitrile; a similar result has previously been obtained for 4-chloroanisole.¹⁰

HCl elimination might be a concerted process assisted by H-bonded configurations involving the excited molecule and its solvent cage. If, on the other hand, a two-step mechanism was to be envisaged, it would most likely consist of Cl⁻ departure followed by deprotonation of the resulting carbocation:



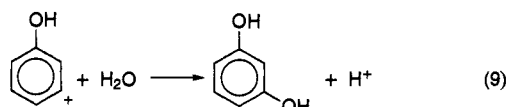
The reason to invoke this sequence rather than deprotonation of the 4-CIP excited state followed by Cl⁻ elimination is the observed lack of a pH effect on the carbene yield between pH 0 and 7, whereas $\text{p}K^*(\text{S}_1)$ values of phenols generally lie around 4²⁶ and $\text{p}K^*(\text{T}_1)$ values do not significantly differ from their ground-state counterparts. The deprotonation step must therefore concern a much more acid species, and this might be the 4-hydroxyphenyl cation; in this connection, the very high acidities of phenol radical cations ($\text{p}K_a \approx -2$ ²⁷) have to be

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recalled. Almost complete quenching of hydroquinone formation upon addition of 1.2 M methanol (Table 1) without concomitant appearance of the insertion product, 4-methoxyphenol, furthermore indicates that the reactions involved occur at the carbene and not at the cation level; deprotonation of the cation must therefore be assumed to be much faster than its reaction with either water or the alcohol. This behavior is in contrast with that of substituted diphenylcarbenes, which show a marked protonation tendency in their singlet state.²⁸

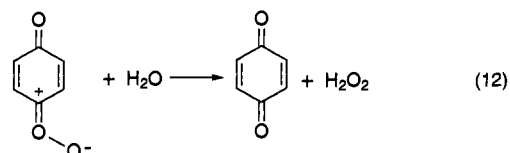
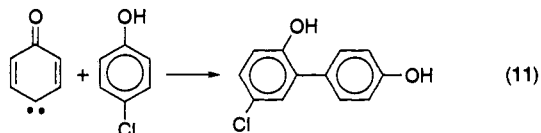
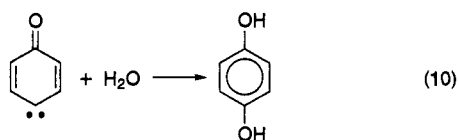
The two-step mechanism is further supported by the observation that one-photon photolysis of 3-chlorophenol does not lead to any observable transients on a time scale of 50 ns, whereas product analysis of this system indicates a clean photosubstitution reaction yielding resorcinol as the only measurable product ($\Phi = 0.09$).²⁹ Since a carbene structure cannot be formed by deprotonation of the 3-hydroxyphenyl cation, the only pathway available for the latter is reaction with water, in agreement with the experimental result:



In contrast, photolysis of 2-chlorophenol appears to involve primary steps that are analogous to those of 4-ClP photolysis. A carbene intermediate (2-oxocyclohexa-3,5-dienylidene) has early been proposed to account for the detection of cyclopentadienic acids as the main products.³⁰ Transient absorption measurements supporting this suggestion will be published elsewhere.

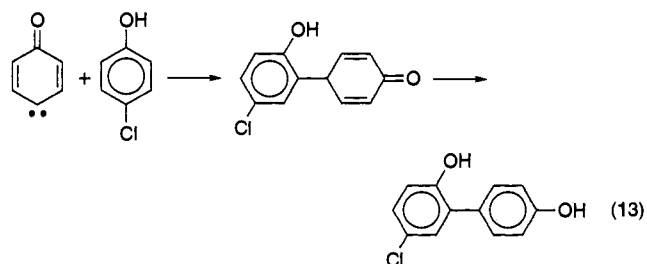
The photochemistry of 4-chlorophenolate differs from that of its undissociated counterpart in two respects: first, the quantum yield of carbene formation is lower by about an order of magnitude; second, one-photon photoionization with formation of hydrated electrons and 4-chlorophenoxy radicals takes place. Both this latter process and the exceedingly small fluorescence yields and lifetimes are characteristic for phenolates.²⁰ The reduced yields of HCl elimination can thus be traced to a competing singlet deactivation process.

2. Photoproduct Formation. The observation of H^+ and Cl^- as ubiquitous products of 4-chlorophenol photolysis demonstrates that photolysis indeed involves HCl elimination (reactions 1–4). The formation of the other observed products can easily be accounted for if 4-oxocyclohexa-2,5-dienylidene and, following its reaction with O_2 , benzoquinone *O*-oxide are assumed as intermediates:



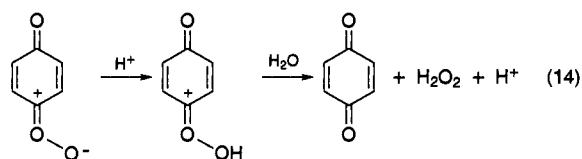
Reaction 10—and further possible carbene reactions involving 4-chlorophenol—account for the fact that product yields as well as the quantum yield of 4-chlorophenol disappearance are concentration dependent (Figure 9).

Reactions 9 and 10 must involve intermediates bearing the cyclohexa-2,5-diene-4-one moiety, subsequent H migration being required for end product formation, e.g.:



This intermediate is a likely candidate for assignment of the long-lived 395 nm transient observed in argon-saturated solutions. As noted above, however, further as yet unidentified products are likely to be formed by reaction of photoproduct intermediates with 4-chlorophenol, which could also contribute to this transient.

Formation of *p*-benzoquinone formally involves abstraction of an O atom from benzoquinone *O*-oxide (reaction 11). The pH dependence of the decay rate constant of the oxide demonstrates the ionic character of this reaction, with the possible intermediacy of a protonated intermediate:



This mechanism also explains the acceleration of oxide decay in neutral solution with increasing pulse energy; in this case, H^+ ions produced in the photolysis step itself are the cause.

In the presence of an alcohol, phenol is found as the main product. Formation of 4-methoxyphenol is minor, which shows that reaction 5 does not efficiently proceed by insertion of the carbene into the alcohol O–H bond. Detection of phenol as well as of dihydroxybiphenyls can be understood as consequences of phenoxy radical reactions.

2,5,4'-Trihydroxybiphenyl is found as a secondary product of 4-chlorophenol photolysis. Its yield increases nonlinearly with absorbed dose, the limiting yield being zero. It very likely arises from excitation of 5-chloro-2,4'-dihydroxybiphenyl by a mechanism that is analogous to the formation of hydroquinone from 4-chlorophenol. The occurrence of this process has already been demonstrated¹⁶ by direct irradiation of 5-chloro-2,4'-dihydroxybiphenyl.

3. Structural and Spectroscopic Properties of 4-Oxocyclohexa-2,5-Dienylidene: Semiempirical Calculations. The high quantum yield of 4-oxocyclohexa-2,5-dienylidene formation by 4-chlorophenol photolysis opens the way to the study of its properties, and thereby to what may be the first opportunity to study the reactivity of an aromatic carbene in aqueous solution. Some relevant reactions are described below; in this section, we describe the results of semiempirical calculations carried out to allow a better understanding of their mechanism.

Calculations were performed within the AM1 parametrization as supplied by the MOPAC 6.0 semiempirical package.³¹ Two

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methods were employed, based either on use of the UHF open shell Hamiltonian or on calculations carried out within the closed shell RHF scheme including configuration interaction using all 100 microstates which can be constructed from five effective orbitals, i.e. the three highest occupied and the two lowest unoccupied ones; this was done in order to allow comparison of energies with those of open shell systems where the configuration interaction was built from the two highest doubly occupied, two singly occupied, and the lowest unoccupied orbitals.

A planar triplet ground state was obtained by both methods upon geometry optimization; the carbene belongs to the C_{2v} point group, in good agreement with recent *ab initio* UHF calculations.^{22b} The ground state of the carbene is thus characterized by two nearly degenerate singly occupied orbitals: the HOMO has b_1 symmetry and is constructed from the C_4 p_x orbital (C_4 being the carbon atom in *para* position to the oxygen) in conjugation with the π orbitals of the two double bonds; the next lowest HOMO-1 conforms to the a_1 representation and it is identical to the p_z orbital on C_4 (along the C_2 axis of the molecule). As these orbitals are nearly degenerate, the triplet, of B_1 symmetry, is the lowest state, 3800 cm^{-1} below the lowest singlet. The bond order matrix gives a partly double-bonded character for the C_3 - C_4 and C_4 - C_5 bonds, with a bond order of 1.31 in both cases. The bond orders for the other carbon-carbon bonds are 1.47 (C_2 - C_3) and 1.01 (C_1 - C_2).

Two low-lying electronic transitions were obtained at 630 and 520 nm. The latter is symmetry-forbidden as it corresponds to a $b_2 \rightarrow b_1$ excitation, where the b_2 is an oxygen lone pair. Weak absorption bands were indeed found between 500 and 570 nm by matrix isolation spectroscopy,^{22b,c} and at 580 nm in the present study. The prominent double peak excitation in the near-UV (Figure 1 and 6) is nicely reproduced by the calculations which yield two triplet-triplet transitions peaking at 358 and 353 nm. Various excitations were obtained at higher energies (200-300 nm).

The p_z orbital of C_4 may thus be considered as the frontier orbital in most reactions as it is strongly localized but singly occupied. The reactivity of the carbene should accordingly resemble that of R_3C^\bullet radicals, in contradistinction to aliphatic carbenes which possess two equivalent singly occupied p -orbitals.³² Addition of O_2 to the C_4 p_z orbital yields benzoquinone *O*-oxide, which results as a stable species (heat of formation 11.38 kcal/mol compared to the UHF energies of 54.3 kcal/mol for the carbene triplet and -27.72 kcal/mol for oxygen) in a singlet ground state, 16.6 kcal/mol below a triplet excited state. The lowest energy geometry is planar and the COO angle is nearly 120° . The C-O bond length is determined to 1.42 Å, and that of the O-O bond is 1.17 Å, while a value of 1.25 Å was obtained for the C=O double bond in the 1 position. The charge density on the oxygen atom connected to C_4 is +0.16 whereas the second oxygen is negatively charged (-0.19). The O-O bond is thus strongly polarized.

4. 4-Oxocyclohexa-2,5-dienylidene Reactivity. The kinetic data of 4-oxocyclohexa-2,5-dienylidene reactions determined in the present work are summarized in Table 2.

Rate constants were measured by transient absorption spectroscopy, monitoring either the decay of the carbene at $\lambda = 384$ or 250 nm or the buildup of the reaction product. In each case, the kinetics were studied over a range of reactant concentrations (cf. Figures 4 and 5).

(a) Reaction with O_2 . In agreement with a previous determination carried out in a nonpolar solvent,²² the rate constant for reaction with O_2 is found to be close to the

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Table 2. Rate Constants for Reaction of 4-Oxocyclohexa-2,5-dienylidene with Various Reactants in Aqueous Solution^a

reactant	k ($M^{-1} s^{-1}$)	method
4-chlorophenol	1.5×10^8	A
H_2O	1.5×10^3	A
O_2	3.5×10^9	B
Cl^-	$< 3 \times 10^5$	C
Br^-	6.8×10^7	C
I^-	4.6×10^9	C
methanol	1.0×10^6	D
ethanol	6.4×10^6	D
1-propanol	9.3×10^6	D
2-propanol	1.7×10^7	D
1-butanol	1.7×10^7	D
2-butanol	1.9×10^7	D
<i>tert</i> -butyl alcohol	5.0×10^5	D
acetonitrile	2.5×10^5	D

^a Methods used for determination of rate constant: (A) carbene decay at $\lambda = 250$ nm; (B) buildup of benzoquinone *O*-oxide at $\lambda = 460$ nm; (C) carbene decay at $\lambda = 384$ nm; (D) buildup of phenoxyl radical at $\lambda = 400$ nm.

diffusion-controlled limit, in accordance with the fact that the carbene reacts from a triplet state. Similar results have been obtained for formation of a range of diaryl carbonyl oxides.³³ There is a single well-defined pathway for this reaction, as witnessed by quantitative formation of benzoquinone in oxygen-saturated solution (Table 1).

(b) Reaction with Halides. The decay kinetics of the carbene at 384 nm were used to determine the rate constants of its reactions with Cl^- , Br^- , and I^- . No product of this reaction could be detected by transient absorption spectroscopy, indicating that it proceeds by direct addition to the carbene. The rate constant increases by about two orders of magnitude in each step of the sequence $Cl^- < Br^- < I^-$. This large effect may be caused by the influence of ionic radius as well as that of a heavy-atom effect reflecting the triplet character of the carbene. The results obtained by transient spectroscopy are complemented by those of product analysis, which document facile substitution of Cl by Br in the photolysis of 4-chlorophenol in the presence of Br^- , but a more reluctant opposite effect in the photolysis of 4-bromophenol in the presence of Cl^- .

(c) Reaction with Alkanols and Other Alkane Derivatives. The respective rate constants increase, for linear alkanols, with chain length (Table 2). The rate constant for reaction with methanol is close to that previously determined in Freon-113.²³ The kinetic behavior outlined in Table 2 parallels that, for instance, of H atoms toward alkanols³⁴ and reflects considerably lower reactivity toward α -hydrogens; this is most visible in the particularly low rate constant with *tert*-butyl alcohol. As mentioned above, the experimentally determined yield of the insertion product with methanol, 4-methoxyphenol, is very small; this underlines a pronounced preference of H abstraction over insertion. A slow H abstraction reaction was even noticed with acetonitrile in aqueous solution. Reactivity of the carbene toward alkanols thus underlines the biradicaloid character of this species, again consistent with its triplet electronic structure,³⁵ and in agreement with the conclusions drawn from the semiempirical calculations as discussed above. The phenoxyl radicals formed in the reaction have no measurable tendency to couple with the parent alkanol radicals; this is shown by the absence of the coupling product, 4-hydroxybenzyl alcohol, among the products determined upon photolysis in the presence of methanol.

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(d) **Reaction with 4-Chlorophenol.** As discussed above, reaction of the carbene with 4-chlorophenol itself yields, among other, non-identified products, the coupling product 5-chloro-2,4'-dihydroxybiphenyl (reaction 12). Formally, this process corresponds to insertion of the carbene into an aromatic C–H bond. The rate constant of $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ appears too high for insertion of a triplet carbene, however; a two-step mechanism consisting of H abstraction followed by radical coupling (phenoxyl with, e.g., 2-hydroxy-5-chlorophenyl) might be envisaged as an alternative. The radical combination step would have to be fast since the phenoxyl radical is not detected in the transient spectrum (Figure 1); consequently, a rather efficient intersystem crossing in the triplet radical pair would have to be assumed, possibly assisted by the presence of a Cl atom in one of the radicals, in contrast to the situation prevailing in reaction of the carbene with alkanols.

(e) **Reaction with H₂O.** The rate constant of this reaction was determined by two methods: the limiting value of carbene decay at zero 4-chlorophenol concentration (Figure 4) on the one hand, and the influence of 4-chlorophenol concentration on hydroquinone formation as measured by product analysis (Figure 9, insert) on the other. In the second case, a ratio of 10^5 between the rate constants with 4-chlorophenol and with water can be deduced from the slope, in good agreement with the result of the first method. The reaction formally corresponds to carbene insertion into an O–H bond of a water molecule. One possible mechanism would consist of H abstraction from H₂O followed by recombination of the phenoxyl radical with the remaining OH radical. Again, the phenoxyl radical is absent in the transient spectrum. An attempt was made to scavenge eventual OH radicals with SCN[−] (0.01 M), which does not measurably react with the carbene at this concentration. This attempt was unsuccessful; neither did addition of SCN[−] influence the hydroquinone yield nor was it possible to detect formation of (SCN)₂-radical anions by transient spectroscopy. Unless the recombination reaction should be too rapid to allow OH scavenging, this result indicates that the barrier for O–H rupture is too high to make this pathway possible and that reaction of the carbene with H₂O indeed proceeds by insertion.

More information concerning the exceptional stability of the carbene in water is provided by semiempirical calculations. Contrary to the addition reaction with molecular oxygen which is found to be exothermic, all considered interactions with H₂O are strongly repulsive. Although the products of insertion into the H–OH bond have low energy, high barriers have to be overcome to attain them, resulting from the large O–H binding energy. Moreover, a specific mode of interaction between the carbene and a water molecule is provided by overlap of the singly occupied p_z with the doubly occupied oxygen lone pairs. In spite of the questionability of semiempirical computations of intermolecular interactions, the calculation in this case actually yields a local minimum at a C₄–O distance of 1.45 Å. This particular effect should additionally increase the activation barrier for reaction, but more importantly it could lead to an orientation of the hydroxy moiety that is unfavorable in view of an insertion reaction.

The observed lack of reactivity of 4-oxocyclohexa-2,5-dienylidene with respect to insertion into O–H bonds thus seems to be due to specific structural reasons besides the spin restrictions imposed by the triplet character of the carbene ground state. This might explain why reaction does not measurably take place in competition with intersystem crossing in the carbene singlet after its formation from excited 4-chlorophenol, in contrast to what has been observed for diphenylmethylenes.³⁶ Once the

carbene triplet is formed, thermal repopulation of the singlet is bound to be inefficient due to the relatively large triplet–singlet energy difference. Still, reaction with H₂O might proceed from the thermally populated singlet, possibly assisted by stabilization of the latter in a polar environment as recently suggested for 1,2-diphenyl-1-butylydene,³⁷ the presence of a small quantity of the insertion product, 4-methoxyphenol, among the products formed in the presence of methanol (Table 1) may be taken as an indication of the possibility of a singlet pathway.

Conclusions

The puzzle of the mechanism of aqueous 4-chlorophenol photolysis thus finds a rather unexpected solution. Not only did transient absorption spectroscopy definitely prove the heterolytic character of this process, but it also unveiled the formation of the carbene, 4-oxocyclohexa-2,5-dienylidene, by HCl elimination from the substrate. The final phototransformation products are easily accounted for by the reactions of this carbene; in particular, formation of *p*-benzoquinone in the presence of O₂ can now be explained by its addition to the carbene, yielding benzoquinone *O*-oxide, which is also identified by its transient spectrum.

Beyond its intrinsic interest in the framework of the study of the photochemistry of aryl halides, photolysis of 4-chlorophenol offers a simple and straightforward opportunity to produce and study, in an aqueous environment, a carbene which previously had been accessible in cryogenic matrices or inert nonpolar solvents only. The present study indeed may be the first one of a carbene in a pure aqueous solution, and it yields the quite unexpected result of an exceptional stability, characterized by a half-life of 8.6 μs in the absence of other reactants. Specific reactions of the carbene with added substrates are therefore accessible for kinetic investigation. The reactivity pattern emerging from our results clearly demonstrates the triplet character of the carbene, leading to H abstraction from alkanols and addition to O₂ and halides with strong indication of a heavy-atom effect in the latter case. The low rate constant for reaction with H₂O, on the other hand, may be explained by the fact that radical dissociation is prohibited by a high activation barrier, leaving an insertion mechanism as the only possibility.

Experimental Section

All chemicals were of the highest available purity (Aldrich or Fluka). 4-Chlorophenol, 3-chlorophenol, and *p*-benzoquinone were further purified by vacuum sublimation. 5-Chloro-2,4'-dihydroxybiphenyl and 2,5,4'-trihydroxybiphenyl were synthesized as described earlier.¹⁶ Triply distilled water and reagent or spectroscopic grade non-aqueous solvents were used for preparation of solutions.

A frequency-quadrupled Nd:YAG laser (Quanta-Ray DCR-1, pulse duration 7 ns, λ_{exc} = 266 nm) was used as a light source in transient absorption measurements. The frequency-doubled output of a pulsed dye laser (Spectra-Physics PDL-3) pumped by the Nd:YAG laser was used alternatively for some experiments at λ_{exc} = 280 nm. Transient absorption spectroscopy was carried out in a right-angle geometry with both photolysis and analysis beams being defined by rectangular apertures. The area irradiated by the laser pulse was 0.0416 cm²; 1 mJ/pulse therefore corresponds to 24 mJ cm^{−2}. A ballistic calorimeter (Raycon-WEC 730) was employed for measurement of laser pulse energy. The time resolution of transient absorption measurements was typically 50 ns. All experiments were carried out at ambient temperature. More details about experimental setup and techniques have been published elsewhere.^{18b}

Variation of O₂ concentration in transient absorption experiments was performed by saturating the solution with a mixture of O₂ and argon and measuring the O₂ concentration *in situ* by its effect on

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the decay rate constant of e_{aq}^- produced by photoejection from $Fe(CN)_6^{4-}$ in aqueous solution.

Fluorescence lifetimes were measured by a single-photon time-correlated technique as described earlier.³⁸

Continuous irradiations were carried out using a 1600 W xenon arc in conjunction with a high-intensity monochromator (Schoeffel). Potassium ferrioxalate was employed for chemical actinometry.

HPLC analysis was performed on a Beckman chromatograph with UV detection or a Waters chromatograph equipped with a photodiode array detector, using a conventional C_{18} column (250 mm \times 4 mm).

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Hydrogen peroxide was determined by oxidation of Fe^{2+} into Fe^{3+} which was followed spectrophotometrically as the thiocyanato complex. A spectrophotometric method was also used for Cl^- determination.³⁹

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