Photochemistry of substituted 4-halogenophenols: effect of a CN substituent

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The photochemistry of 5-chloro-2-hydroxybenzonitrile **1** was studied in aqueous solution using transient absorption spectroscopy and product analysis. The triplet carbene 3-cyano-4-oxocyclohexa-2,5-dienylidene **2** (λ_{max}/nm 385, 368) was successfully detected and identified on the basis of its characteristic reactivity. This transient species is converted into cyanobenzo-1,4-quinone-*O*-oxide (λ_{max}/nm 470) by reaction with oxygen and is reduced into 2-cyanophenoxyl radical (λ_{max}/nm 402, 387) by propan-2-ol. The product studies confirm the intermediary formation of carbene **2**. 2,5-Dihydroxybenzonitrile **3** and the biphenyls **4** and **5** are primary photoproducts in deoxygenated solutions whereas 2-hydroxybenzonitrile **9** and 5-bromo-2-hydroxybenzonitrile **10** are cleanly produced upon addition of propan-2-ol (0.13 M) and bromide ions (10^{-2} M), respectively. In oxygen-saturated solutions, cyanobenzo-1,4-quinone **8** is the main photoproduct. The quantum yield of carbene formation (0.062) is reduced by 40% in the presence of oxygen and is increased up to a value of 0.20 upon addition of bromide or iodide ions. These results can be interpreted in terms of triplet quenching and heavy-atom enhancement and support the assumption that the carbene **2** is formed from the triplet excited state of **1**; this assumption is supported by a detailed study of the phototransformation of **1** in ethanol. Mono- and biphotonic formations of solvated electrons and 4-chloro-2-cyanophenoxyl radicals (λ_{max}/nm 427, 408) are also observed from neutral **1**. The effects of CN substitution can be traced to deprotonation of the lowest excited singlet state on the one hand ($pK^* = 0.12 \pm 0.04$) and to an increase of the triplet lifetime on the other.

Introduction

Halogenophenols exhibit an interesting photoreactivity in aqueous solution (see refs. 1 and 2 for reviews). In the case of 4-halogenophenols, heterolytic photoelimination of the halogen in polar protic solvents leads to formation of the carbene 4-oxocyclohexa-2,5-dienylidene (λ_{max}/nm 370, 384) whose lifetime in water is long enough for detection on the microsecond timescale.[3] This carbene can be trapped by oxygen with formation of benzo-1,4-quinone-*O*-oxide (λ_{max}/nm 460),[4,5] can add on the starting 4-halogenophenol with production of adducts (λ_{max}/nm 405)[3] and can abstract an H-atom from alcohols yielding the phenoxyl radical (λ_{max}/nm 385, 400).[3] In the case of 4-chlorophenol, the quantum yield of the carbene formation is very high (0.75). All the photoproducts observed under continuous irradiation (hydroquinone, benzo-1,4-quinone, coupling products and phenol) can be understood from the reactions of the carbene with water, oxygen, the starting halogenophenol and H-donor molecules. The carbene exhibits triplet reactivity; it was assumed to be formed directly from the triplet excited state of the 4-halogenophenol,[3] but no experimental evidence could be presented in favour of this assumption. Alternatively, it might be proposed that the carbene is initially formed in the singlet state and is then converted into the triplet by rapid intersystem crossing. However, how efficient this intersystem crossing step would have to be is easily seen from the fact that singlet carbenes very efficiently insert into the O–H bond of water molecules.

This highly efficient photoreactivity of 4-halogenophenols has subsequently been corroborated by other authors, using Fourier-transform electron spin resonance spectroscopy[6] or nanosecond transient absorption spectroscopy.[7] Recently, the assumption of carbene formation from the triplet excited state of the phenol was questioned[8] on the grounds that the phototransformation quantum yield of 4-halogenophenols decreases when the substituent is changed from fluoro over chloro and bromo to iodo, in contrast to what would be expected on the grounds of an internal heavy-atom effect.

We reasoned that the substitution of 4-halogenophenols by an electroattracting group such as the CN group would change the photoreactivity. First, the substitution of phenols by a CN substituent is known to lower the pK_a values. In particular, 2-hydroxybenzonitrile is a strong acid in the first singlet excited state ($pK^* = 0.66$).[9] Second, the presence of an electroattracting group is expected to hinder the loss of the halide ion and may lengthen the lifetime of the excited states. In the hope of gaining further insights into the mechanism of the carbene formation, we studied the photolysis of 5-chloro-2-hydroxybenzonitrile **1** using transient absorption spectroscopy and product studies techniques.

Experimental

General

5-Chloro-2-hydroxybenzonitrile was purchased from Maybridge (England) and was recrystallized from water prior to use. Water was purified with a Milli-Q (Millipore) device. All other reagents were used as received. ^{1}H NMR spectra were recorded on a Bruker AC400 spectrometer. Mass analyses were performed by the Service d'analyse of the Université d'Orléans, France. Ammonia was used for chemical ionisation mass spectra. UV–visible spectra were recorded on a Cary 3 (Varian) spectrophotometer. Analytical HPLC was carried out on a Waters apparatus equipped with a photodiode array detector and a conventional reverse phase 5 µm column. The following eluting gradient was used: from 0 to 30 min mixture water with H_3PO_4 (0.1%)–MeOH (55:45, v/v) then at 35 min mixture water with H_3PO_4 (0.1%)–MeOH (30:70, v/v). Preparative HPLC was performed on a Gilson apparatus with UV detection using a semi-preparative microsorb 3 µm column and water–methanol mixtures (55:45, v/v) and (30:70, v/v) as eluents. Chloride ions were titrated using a Waters Quanta 4000 capillary HPLC equipped with a capillary column (0.75 µm, 0.06 m). The electrolyte was CrO_4^- and surfactant Waters OFM-OH$^-$. The pK_a of the ground state **1** was evaluated by a spectrophotometric method. Phosphate buffers (6×10^{-3} M) were used to adjust the pH within the range 5.67–6.96 and $HClO_4$ and NaOH to adjust the pH at 3 and 12. The pK_a was computed using the relationship: $pK_a = pH + \log(A_b - A)/(A - A_a)$, where A_b, A_a and A are absorbances measured at 336 nm in solutions at pH = 12, 3 and at variable pH, respectively.

Fluorescence measurements

A Perkin-Elmer MPF-3L spectrofluorimeter equipped with an IP 28 photomultiplier was used for the fluorescence measurements. Fluorescence spectra were recorded using solutions of **1** at a concentration of 10^{-4} M. The pH was adjusted with $HClO_4$ or NaOH solutions. The Hammett acidity scale H_0 was used instead of the pH scale[10] when $HClO_4$ concentrations exceeded 0.1 M. Phenol (10^{-3} M) was used as the standard ($\Phi_f = 0.13$ at 300 K)[11] for the evaluation of fluorescence quantum yields. All measurements were made at room temperature. Fluorescence lifetimes were measured by a single-photon-correlated technique as described earlier.[12]

Nanosecond laser flash photolysis

Transient absorption experiments were carried out using a frequency-quadrupled Nd:YAG laser (Quanta-Ray DCR-1, 266 nm, pulse duration 10 ns). The procedures used for transient absorption spectroscopy measurements have been described previously.[3,13] For some experiments requiring low pulse energies (P/mJ < 0.1), the excitation wavelength was set at 280 nm using the frequency-doubled output of a parametric oscillator (Lambda Physik Scanmate OPPO) pumped by the third harmonic of an Nd:YAG laser (Coherent Infinity).

Steady-state irradiations

For quantum yield measurements and analytical runs, photolyses were carried out at 313 nm using a Bausch and Lomb monochromator equipped with a high pressure mercury lamp (200 W). Potassium ferrioxalate was used as chemical actinometer. Measurements were made in triplicate. For preparative separations, samples were irradiated in a device equipped with six sunlamps emitting from 280 to 350 nm with a maximum of emission located at 310 nm. Solutions were deoxygenated by nitrogen or argon bubbling.

Identification of products

Two 100 ml portions of **1** (2×10^{-3} M) were saturated with N_2 for 30 min prior to the irradiation, irradiated for 1 h and finally evaporated to 20 ml. Four photoproducts were isolated by preparative HPLC. The assignments were based on ^{1}H NMR and mass spectra.

2-Hydroxy-5-chloro-6-(3′-cyano-4′-hydroxyphenyl)benzonitrile **4**: λ_{max}/nm (H_2O) 309; δ_H (400 MHz; CD_3OD) 7.13 (1H, d, *J* 9.0, 3-H), 7.25 (1H, d, *J* 8.8, 5′-H), 7.63 (1H, dd, *J* 2.0 and 9.0, 6′-H), 7.71 (1H, d, *J* 2.0, 2′-H), 7.73 (1H, d, *J* 8.9, 4-H); *m*/*z* 270 and 272 (M^+, 50%).

2-Hydroxy-5-chloro-3-(3′-cyano-4′-hydroxyphenyl)benzonitrile **5**: λ_{max}/nm (H_2O) 313 (ε/dm^3 mol^{-1} cm^{-1} 7500 ± 700); δ_H (400 MHz; CD_3OD) 7.20 (1H, d, *J* 8.8, 5′-H), 7.59 (1H, d, *J* 2.6, 4-H), 7.61 (1H, d, *J* 2.6, 6-H), 7.80 (1H, dd, *J* 2.3 and 8.8, 6′-H), 7.90 (1H, d, *J* 2.3, 2′-H); *m*/*z* 270 and 272 (M^+, 100%).

2-Hydroxy-5-(3′-cyano-4′-hydroxyphenyl)benzonitrile **6**: λ_{max}/nm (H_2O) 265, 306; δ_H (400 MHz; CD_3OD) 7.20 (2H, d, *J* 8.7, 3-H and 5′-H), 7.86 (2H, dd, *J* 2.5 and 8.9, 4-H and 6′-H), 7.90 (2H, d, *J* 2.4, 6-H and 2′-H); *m*/*z* 236 (M^+, 50%).

2-Hydroxy-5-chloro-3-(5′,3″-dicyano-6′,4″-dihydroxybiphenyl)ylbenzonitrile **7**: δ_H (400 MHz; CD_3OD) 7.24 (1H, d, *J* 8.8, 5″-H), 7.69 (1H, d, *J* 2.6, 4-H), 7.75 (1H, d, *J* 2.6, 6-H), 7.78 (1H, dd, *J* 2.9 and 8.8, 6″-H), 7.87 (2H, d, *J* 2.9, 2″-H and 4′-H), 7.93 (1H, d, *J* 2.9, 2′-H); CI-NH_3 *m*/*z* 388 and 400 (MH^+, 25%).

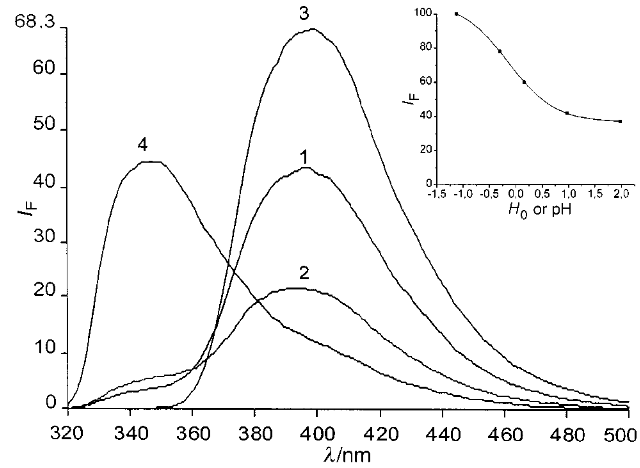


Fig. 1 Emission spectra of **1** 1) in water pH = 4.4; 2) in water pH = 0.8; 3) in water pH = 12; 4) in ethanol. Inset: dependence of the fluorescence intensity measured at 340 nm on pH or H_0. Excitation wavelength set at 315 nm.

Authentic samples of 2,5-dihydroxybenzonitrile **3** and cyanobenzo-1,4-quinone **8** were synthesized using the following procedures. A solution of 2-hydroxybenzonitrile (4.8 g, 0.04 mol), $K_2S_2O_8$ (10.8 g, 0.04 mol) and NaOH (0.8 g, 0.02 mol) was stirred at room temperature for 48 h. 5-Sulfo-2-hydroxybenzonitrile potassium salt was recovered after cooling the solution and was hydrolyzed into **3** upon stirring in hot acidic solution.[14] Finally, **3** was recovered by recrystallization. An acidic mixture of **3** (10 mg, 0.074 mmol) and $NaNO_2$ (14 mg, 0.2 mmol) was stirred for 8 h at room temperature. $NaNO_2$ was extracted with ether and **8** finally recovered after evaporation.

2,5-Dihydroxybenzonitrile **3**: λ_{max}/nm (H_2O) 317 (ε/dm^3 mol^{-1} cm^{-1} 3500 ± 200); δ_H (400 MHz; CD_3OD) 7.00 (1H, dd, *J* 2.9 and 8.4, 4-H), 7.10 (1H, d, *J* 2.9, 6-H), 7.24 (1H, d, *J* 8.4, 3-H); *m*/*z* 135 (M^+, 100%) and 107 ($M^+ - 18$).

Cyanobenzo-1,4-quinone **8**: λ_{max}/nm (H_2O) 254, 446 (ε_{446}/dm^3 mol^{-1} cm^{-1} 1800 ± 200); *m*/*z* 133 (M^+, 100%).

5-Bromo-2-hydroxybenzonitrile **10** was produced by irradiating a deoxygenated solution of **1** (10^{-3} M) containing NaBr (10^{-2} M) at 313 nm for 15 min. After irradiation, the solution was evaporated to dryness. The residue was dissolved in methanol and analyzed by mass spectrometry. *m*/*z* 197 and 199 (M^+, 100%).

Results

Absorption and fluorescence measurements

The maxima of the longest-wavelength (S_1) absorption bands of neutral and anionic **1** are located at λ_{max}/nm 306 (ε/dm^3 mol^{-1} cm^{-1} 3400 ± 100) and λ_{max}/nm 335 (ε/dm^3 mol^{-1} cm^{-1} 4800 ± 200) respectively. The pK_a of the ground state was evaluated as 6.44 ± 0.03. This value is close to that measured for 2-hydroxybenzonitrile (6.97 ± 0.02).[9]

The fluorescence emission spectra of **1** are shown in Fig. 1. The emission maxima are located at λ_{max}/nm 348 for neutral **1** and λ_{max}/nm 396 for anionic **1**. The pH dependence of the fluorescence intensity of neutral **1** is depicted in the inset of Fig. 1. The fluorescence intensity measured at 340 nm decreases as H_0 or the pH is increased from −1.0 to 2.0. A plateau value corresponding to 35% of the intensity measured for $H_0 = -1.05$ is reached at pH = 2. The decrease of fluorescence intensity results from the dissociation of the phenolic group in the lowest excited singlet state after excitation of neutral molecules. From the plateau value, it can be deduced that 65% of the neutral

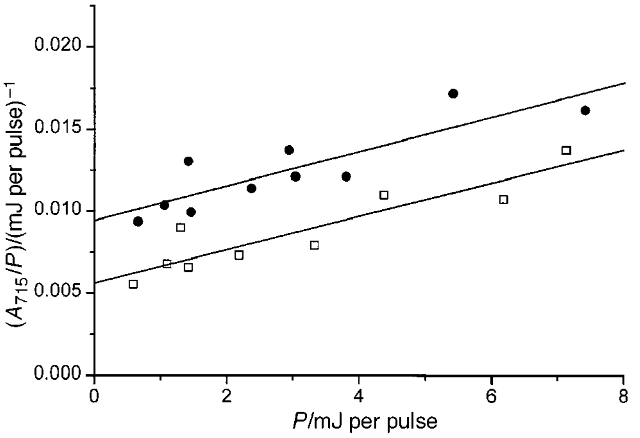


Fig. 2 Hydrated electron formation from **1**: plot of A_{715}/P *versus* P (P = laser pulse energy). All data normalized to the same absorbance (0.5) at the wavelength of excitation. □: pH = 4, ●: pH = 11.

excited state molecules deprotonate at pH values exceeding pH 2. From this pH dependence, the pK_a* of the singlet excited state of **1** was evaluated as 0.12 ± 0.04.

The fluorescence quantum yields were estimated by comparison with the emission of phenol (Φ_f = 0.13 at 300 K).[11] The values obtained for neutral and anionic **1**, respectively, are 0.007 and 0.03. The lifetime of the singlet excited states was evaluated from fluorescence decay measurements as 0.32 ns in ethanol, 0.34 ns in water at pH = 0.8, 0.42 ns in water at pH = 4.4 and 0.52 ns in water at pH = 12.

Laser flash photolysis studies

Formation of hydrated electrons. The characteristic absorption of hydrated electrons was detected at pulse end on excitation of both neutral and anionic **1** with 10 ns pulses (λ_{exc}/nm 266). Since phenolic compounds are susceptible to monophotonic as well as biphotonic ionization processes *via* their S_1 state,[15] the absorbance, A_{715}, at the maximum of e^-_{aq} absorption (λ/nm 715, ε_{715}/M^{-1} cm^{-1} 19000)[16] was monitored as a function of the laser pulse energy, P. Plots of A_{715}/P *versus* P measured for neutral and anionic **1** are linear and parallel (Fig. 2). The linearity of this function is predicted for a mixed one- and two-photon mechanism according to eqn. (1).

$$A_{715} = a \times P + b \times P^2 \qquad (1)$$

The coefficients a and b in this expression are related to the efficiencies of the one- and two-photon ionization processes, respectively. The relatively small value obtained for the coefficient b (the slope of the lines in Fig. 2) is consistent with the short S_1 lifetime of **1**. The one-photon ionization quantum yield can be determined from the coefficient a (the intercepts in Fig. 2) to be Φ = 0.023 ± 0.005 at pH = 4 and Φ = 0.034 ± 0.005 at pH = 11. Φ is lower at pH = 4 than at pH = 11 by 32%; this is in line with the fluorescence-based result that 65% of **1** deprotonate in the S_1 state. Moreover, the observation that the slopes of the regression lines shown in Fig. 2 are parallel indicates that the same excited state absorbs the second photon in the two-photon ionization process, irrespective of the pH value. It can therefore be concluded that ionization of neutral **1** arises from its S_1 state after excited-state deprotonation.

The e^-_{aq} formed by photoionization of **1** decay by a pseudo-first-order reaction with the substrate; the rate constants of this reaction are k/M^{-1} s^{-1} = 1.4 × 10^{10} at pH 4 and 8.6 × 10^{9} at pH 11. As in the case of halobenzonitriles[17] the e^-_{aq} are expected to add to the substrate molecules. In order to check a possible contribution of radical anions of **1** to the transient absorption spectrum, a mixture of **1** and $Fe(CN)_6^{4-}$ was subjected to 266 nm pulses at pH 4. In this system, e^-_{aq} are produced with a quantum yield of the order of 0.5,[18] and radical anions should therefore be generated with the same yield. There was no indication of a corresponding transient at λ/nm > 350.

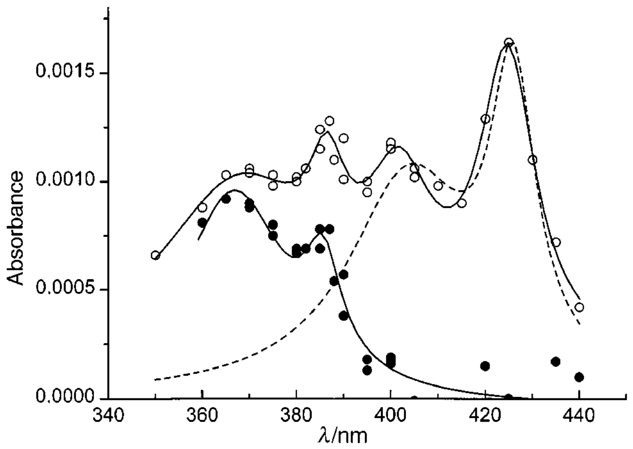


Fig. 3 Transient spectrum (○) measured at pulse end in a deoxygenated solution of **1** (2 × 10^{-3} M) at pH = 4.0; P = 0.56 mJ pulse^{-1}. ●: spectrum obtained after correction for the contribution of the 4-chloro-2-cyanophenoxyl radical (dashed line).

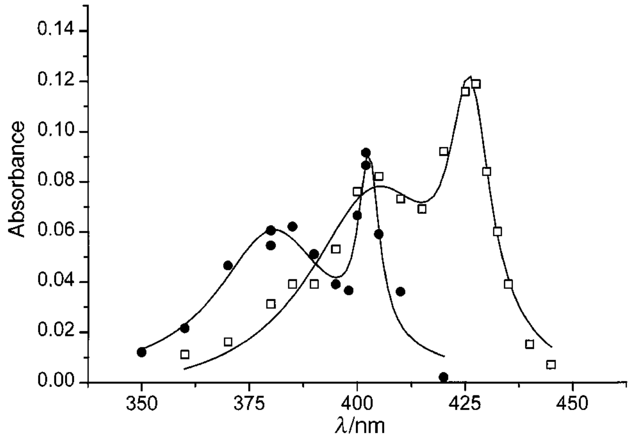


Fig. 4 Absorption spectra of the 4-chloro-2-cyanophenoxyl radical (□) and of the 2-cyanophenoxyl radical (●) produced by photolysis of acidic solutions containing $K_2S_2O_8$ (0.1 M) and **1** or 2-hydroxybenzonitrile (5 × 10^{-4} M, absorbance multiplied by 2.5).

Formation of 4-chloro-2-cyanophenoxyl radicals. The transient spectrum in the near-UV region obtained on laser flash photolysis of **1** at pH values between 1 and 6 is dominated by the strong absorption of anionic **1** arising from excited-state deprotonation and extending up to 350 nm. A search for other photoinduced transients had therefore to be focused on longer wavelengths.

The photolysis of slightly acidic (pH around 4.0) and deoxygenated solutions of **1** (2 × 10^{-3} M) produces at pulse end the transient spectrum shown in Fig. 3. Four maxima appear within the wavelength range 350–440 nm, suggesting the presence of more than one species. Since photoionization will produce 4-chloro-2-cyanophenoxyl radicals concomitantly with e^-_{aq}, this radical is expected to contribute to the overall spectrum. In order to study it independently, we generated it by sulfate radical-induced one-electron oxidation in an acidic solution of $K_2S_2O_8$ (0.1 M) and **1** (5 × 10^{-4} M) irradiated at 266 nm. The resulting radical spectrum, shown in Fig. 4, exhibits two bands at λ_{max}/nm 427, 408 which conform to the two longer-wavelength bands of the overall spectrum in Fig. 3. The 4-chloro-2-cyanophenoxyl radical spectrum, shown as a dashed line in Fig. 3, was then subtracted from the overall spectrum assuming that it is the only species contributing to it at λ/nm > 420. The spectrum remaining after subtraction shows again two maxima, λ_{max}/nm 385, 368.

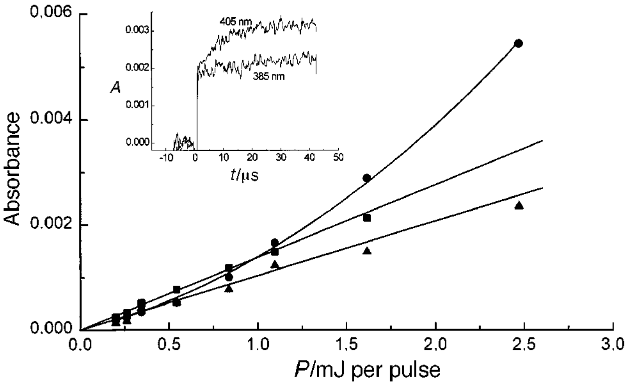


Fig. 5 Pulse energy dependence of absorbances measured in a deoxygenated solution of **1** (2×10^{-3} M) at pH = 4.0. ●: absorbance at 405 nm measured at the end of pulse, ■: absorbance at 405 nm, difference between absorbances measured 40 μs after the pulse and absorbances measured at the end of pulse, ▲: absorbance at 385 nm corrected for the absorbance of the 4-chloro-2-cyanophenoxyl radical. Inset: time course of absorbances at 385 and 405 nm.

Measurements of the dependence of the absorbances at 385 and 405 nm on pulse energy, *P* (Fig. 5) confirmed the hypothesis of two different species absorbing at these wavelengths. At 385 nm, a linear relationship was found as expected for a monophotonic formation process. On the other hand, the absorbance at 405 nm was shown to increase in a nonlinear way with *P*, indicating a biphotonic contribution as expected from the e^-_{aq} formation data (Fig. 2).

Formation and characterization of the carbene 2. The assignment of the residual species present after subtraction of the 4-chloro-2-cyanophenoxyl radical spectrum is aided by the observation that its two-band structure is reminiscent either of a further phenoxyl radical, or of a carbene resulting from a heterolytic dehalogenation step; indeed, the carbene, 4-oxocyclohexa-2,5-dienylidene previously observed as the primary transient following photolysis of 4-chlorophenol[3] spectrally differs from the unsubstituted phenoxyl radical merely by a 16-nm hypsochromic shift. This similarity between the radical and the related carbene reflects the fact that the latter has a triplet ground state giving it a radical-like character.[19]

The only further phenoxyl-type radical that could conceivably arise from photolysis of **1** is the 2-cyanophenoxyl radical. This species was produced using one-electron oxidation of 2-cyanophenol by sulfate radicals and has a two-band spectrum (λ_{max}/nm 402, 387) shown in Fig. 4. The residual transient in Fig. 3 therefore cannot be assigned to a phenoxyl radical; instead, we propose its identification with the carbene **2** resulting from heterolytic dechlorination of **1**.

Characteristic trapping reactions were used to firmly establish the intermediacy of the carbene **2** in the photolysis of **1**. Triplet 4-oxocyclohexa-2,5-dienylidene is known to react with oxygen yielding benzo-1,4-quinone-*O*-oxide.[4,5] This latter species exhibits a broad absorption band with a maximum at 460 nm and decays in a first order reaction with $k_d/s^{-1} = 5.5 \times 10^4$ in neutral medium.[3] As shown in Fig. 6, photolysis of oxygen-saturated solutions of **1** produces a monophotonic transient exhibiting an absorption spectrum (λ_{max}/nm 470) and kinetic characteristics ($k_d/s^{-1} = 8.4 \times 10^4$) very similar to those of benzo-1,4-quinone-*O*-oxide. This transient can therefore be assigned to the cyanobenzo-1,4-quinone-*O*-oxide.

Another reaction characterizing a triplet carbene is its reduction by H-atom donors into a phenoxyl radical.[3,5] The irradiation of deoxygenated solutions of **1** containing propan-2-ol (0.52 M) yields the transient spectra given in Fig. 7. The spectrum obtained in this system exhibits three maxima which can be deconvoluted into the superposition of a 2-cyanophenoxyl radical and a 4-chloro-2-cyanophenoxyl radical; comparison with the spectra of these species (Fig. 4) confirms this assignment. The formation of the 2-cyanophenoxyl radical, which is absent in solutions not containing an H-donor, is explained by rapid reaction of **2** with propan-2-ol. It is interesting to note that the absorption at 425 nm grows in with time to reach a maximum at about 80 μs after the laser pulse; at this time, only 4-chloro-2-cyanophenoxyl radicals are present in the spectrum, indicating conversion of 2-cyanophenoxyl radicals into the former by reaction with **1**.

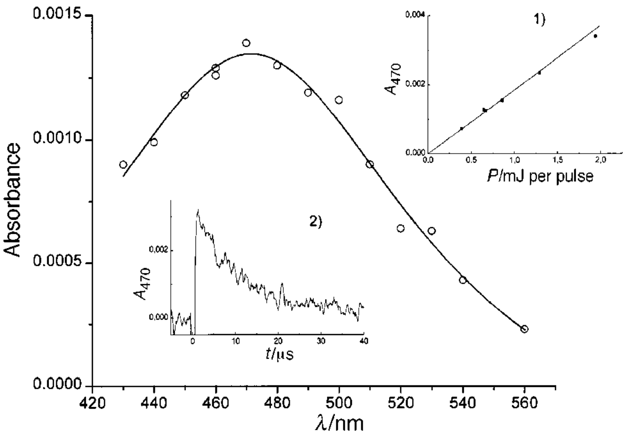


Fig. 6 Transient spectrum measured 200 ns after pulse end in an oxygen-saturated solution of **1** (2×10^{-3} M) at pH = 4.0; *P* = 0.65 mJ pulse^{-1}. Inset 1: dependence of the absorbance measured at 470 nm with *P*. Inset 2: time course of absorbance measured at 470 nm.

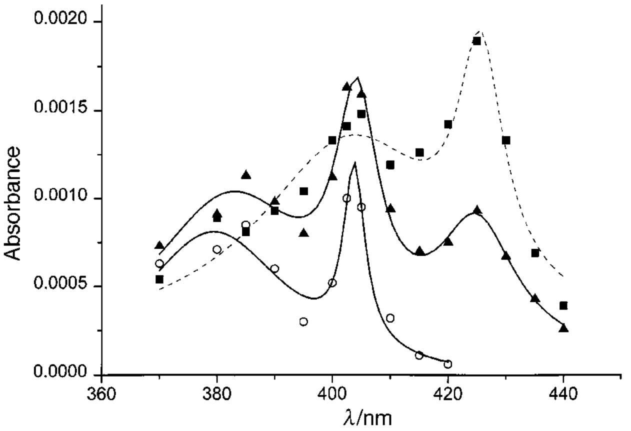


Fig. 7 Transient spectra measured in a deoxygenated solution of **1** containing propan-2-ol (0.52 M); *P* = 0.73 mJ pulse^{-1}. ▲: absorbances measured 500 ns after pulse end, ○: absorbances measured 500 ns after pulse end and corrected for the absorption of the 4-chloro-2-cyanophenoxyl radical, ■: absorbances measured 80 μs after the pulse.

A further transient species appears in slightly acidic deoxygenated solution of **1** when the time course of the absorbance is monitored at 405 nm. This latter transient grows in within 40 μs following the pulse (see the inset of Fig. 5) and is produced by a monophotonic process as shown by the linear dependence on pulse energy (Fig. 5). This species has a lifetime in the millisecond range and probably represents a product formed as a consequence of addition of the carbene **2** on **1**, although it is probably not the immediate product of this addition. A transient of this type has also been observed in the photolysis of 4-chlorophenol.[3]

Transients in ethanolic solution and triplet quenching studies. Flash photolysis of **1** in deoxygenated ethanol leads to the appearance of a short-lived transient with a broad absorption spectrum shown in Fig. 8 (Spectrum A). This transient cannot be observed in O_2-saturated solution and reacts with acrylamide with a rate constant of 2×10^8 M^{-1} s^{-1}; it is therefore assigned to the triplet state of **1**. In the absence of quenchers,

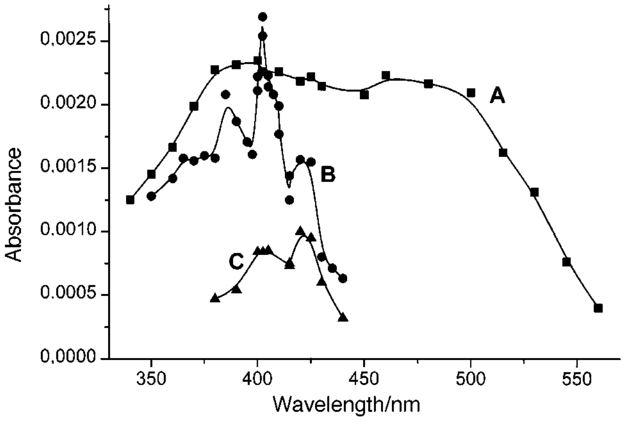


Fig. 8 Transient spectra measured in a solution of **1** (4.75×10^{-3} M) in ethanol (0.4 mJ pulse^{-1}). ■: absorbance measured 100 ns after pulse end in deoxygenated solution, divided by factor 5, ●: absorbance measured 5 µs after pulse end in deoxygenated solution, ▲: absorbance measured 100 ns after pulse end in O_2-saturated solution.

the triplet signal decays with a rate constant of 1.4×10^6 s^{-1}, independently of the substrate concentration.

A triplet energy transfer experiment was conducted as a test of this interpretation. In an ethanolic solution of **1** (1.5×10^{-3} M) containing 2.75×10^{-4} M anthracene, triplet energy transfer from **1** to anthracene was observed, yielding an intersystem crossing yield of 0.60 for **1**, assuming that the transfer is quantitative.

After decay of the triplet signal, a long-lived absorption remains which in deoxygenated solution is similar to that obtained from photolysis of **1** in aqueous solution in the presence of an alcohol (Fig. 7). Again, a sharp maximum at 402 nm witnesses the formation of the 2-cyanophenoxyl radical resulting from dehalogenation of **1**. A smaller band at 425 nm can be assigned to a contribution from the 4-chloro-2-cyanophenoxyl radical. It can therefore be assumed that the photochemistry of **1** proceeds in the same way in aqueous and in ethanolic solutions; the same observation has been made before in the study of the photochemistry of 4-chlorophenol.[3]

The possibility of observing the triplet state of **1** in ethanolic solution opened the way to studying its role in the formation of the photoinduced transients. As shown in Fig. 8, the transient spectrum obtained in O_2-saturated solution consists only of the 4-chloro-2-cyanophenoxyl radical; the contribution from the 2-cyanophenoxyl radical is absent.

The lack of formation of the 2-cyanophenoxyl radical in O_2-saturated solution could be due to quantitative trapping of the carbene **2** by O_2, thus preventing H transfer from ethanol to the carbene. This does not however seem to be the case because there is no sign of the absorption of the cyanobenzo-1,4-quinone-*O*-oxide which should result from this reaction, and which is indeed easily observed in solutions of 4-chlorophenol in alkanols.[3] It must therefore be concluded that quenching of the triplet state also quenches the formation of the photoproducts.

The relationship between triplet and photoproduct absorption was further investigated by studying the pulse energy dependence of laser-induced absorptions in deoxygenated solutions at two wavelengths corresponding to the maximum of the 2-cyanophenoxyl absorption (402 nm) on the one hand, and to the nearest wavelength to the red where this radical does not significantly absorb any more (415 nm). It can be seen from Fig. 8 that both the triplet–triplet and the 4-chloro-2-cyanophenoxyl absorption do not significantly change in this wavelength interval. The results of this experiment are shown in Fig. 9. The long-lived radical absorption is consistently higher at 402 nm than at 415 nm, demonstrating the contribution of the 2-cyanophenoxyl radical. As seen before in aqueous solution (Fig. 5), a marked departure from linearity reflects the two-photon character of the photoionization process at both wavelengths. The short-lived absorption measured at pulse end, however, does not show this difference between the two measuring wavelengths. It can be concluded from this observation that the absorption of the 2-cyanophenoxyl radical is not present at short times after the pulse, in agreement with the hypothesis that it is formed concomitantly with the decay of the triplet state of **1**.

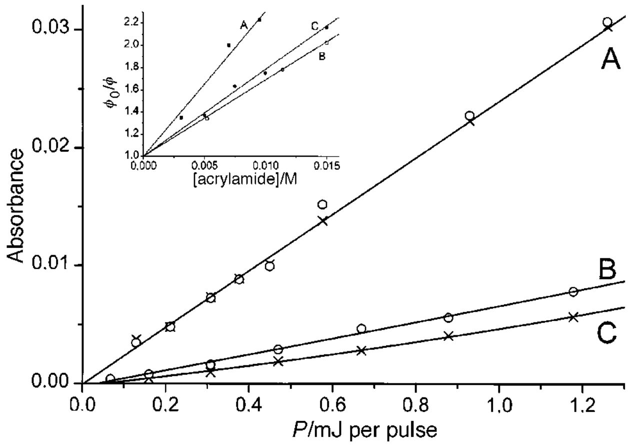


Fig. 9 Pulse energy dependence of transients measured in a deoxygenated solution of **1** (4.75×10^{-3} M) in ethanol. (A) absorbance measured 100 ns after pulse end at 402 nm (O) and 415 nm (X), (B) absorbance measured 5 µs after pulse end at 402 nm, (C) absorbance measured 5 µs after pulse end at 415 nm. Insert: Stern–Volmer plots for the quenching of 2-cyanophenoxyl radical formation by acrylamide (A) in aqueous solution (pH 4) containing 0.26 M propan-2-ol, (B) in aqueous solution (pH 4) containing 0.52 M propan-2-ol, (C) in ethanolic solution.

The influence of the triplet quencher acrylamide on the formation of the 2-cyanophenoxyl radicals was examined in order to subject this hypothesis to a further test. As seen in the insert in Fig. 9, the radical yield diminishes with increasing acrylamide concentration in accordance with a Stern–Volmer relationship, yielding $k_q\tau$/M^{-1} 80 for the product of the quenching rate constant and the lifetime of the quenched state in the absence of the quencher. Since k_q/M^{-1} s^{-1} 1.9×10^8 could be determined by measurement of triplet decay, τ/ns 420 results from the Stern–Volmer treatment, in good agreement with the lifetime of the triplet state in deoxygenated solution (490 ns) as determined from the triplet decay. This result directly confirms that the cyanophenoxyl radicals originate from the triplet state of **1**.

The same experiment, *i.e.* acrylamide quenching of 2-cyanophenoxyl radical formation, was also conducted in deoxygenated aqueous solutions containing two concentrations of propan-2-ol (0.26 and 0.52 M). As in the ethanolic solution, the data show Stern–Volmer behaviour, but the slopes depend on the concentration of propan-2-ol (see the insert in Fig. 9); the values obtained are $k_q\tau$/M^{-1} 128 at 0.26 M propan-2-ol and $k_q\tau$/M^{-1} 70 at 0.52 M propan-2-ol. This indicates that in the case of the aqueous solution the acrylamide interacts with a precursor of the 2-cyanophenoxyl radical that also reacts with the alcohol; this is most likely the carbene. Triplet quenching by acrylamide is of minor importance, probably due to the fact that the triplet lifetime is considerably shorter in water than in ethanol; this is supported by the fact that it was not possible to detect a triplet–triplet absorption in aqueous solution, and by the observation that photolysis is only partially suppressed by O_2 saturation (see below). Assuming $k_q\tau$/M^{-1} < 20 for triplet quenching by acrylamide and k_q/M^{-1} s^{-1} 1.9×10^8 as in ethanolic solution, a triplet lifetime τ/ns < 100 can be estimated for the aqueous medium. In ethanolic solution, interaction of acrylamide with the carbene is unlikely because the lifetime of the latter can be estimated to be about 5 ns if the rate constant for its reaction with ethanol is assumed to be similar to that measured in the 4-chlorophenol system (k/M^{-1} s^{-1} 6.4×10^6).[3]

Steady-state irradiations

Photolysis in deoxygenated medium. The typical HPLC chromatogram of a deoxygenated and slightly acidic solution of **1** irradiated at 313 nm at a conversion extent of 20% is shown in Fig. 10. The main photoproducts are cyanohydroquinone, **3** and the biphenyls **4**, **5** and **6**. The terphenyl **7** is additionally formed when the concentration of **1** exceeds 2 × 10^{-3} M. Small amounts (between 2 and 4%) of cyanobenzo-1,4-quinone **8** are found even in deoxygenated solutions in slightly acidic, neutral or basic solution.

Quantum yields of the photodegradation of **1** and chemical yields of **3**, **5** and of chloride ions in deoxygenated medium are given in Table 1. The quantum yield of the disappearance of **1**, Φ_1, is 0.08 ± 0.01 in slightly acidic medium and about half this value in basic medium. Chloride ions are produced with a smaller quantum yield (0.056 in acidic medium). This difference can be explained by the formation of coupling products between photoproduced transients such as **2** on the one hand and **1** on the other. Of the yields of these coupling products, only that of **5** could be determined; the product balance is therefore not quantitative. The chemical yield of **3** is concentration-dependent: it shows a decrease from 16 to 10% when the concentration of **1** is increased from 2.5 × 10^{-4} to 1.0 × 10^{-3} M. Acidification of the solutions favours the formation of **3** and suppresses that of **8** indicating that the oxidation product **8** is produced by thermal oxidation of anionic **3** during the sampling. The main coupling product is **5**, accounting for 32 to 38% of converted **1**.

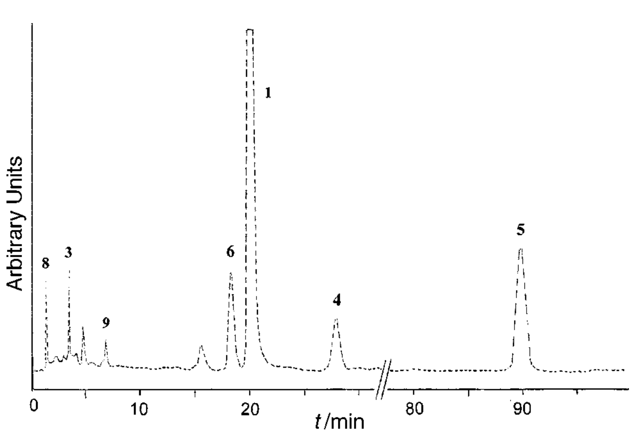


Fig. 10 HPLC chromatogram of a deoxygenated solution of **1** (5 × 10^{-4} M) irradiated for 15 min at 313 nm. Detection set at 230 nm.

Table 1 Photolysis of **1** in deoxygenated medium. Quantum yield of **1** photolysis (Φ_1), quantum yield of chloride ion formation (Φ_{Cl^-}) and chemical yields of photoproducts **3** and **5**

[**1**]/M	pH	Φ_1	Φ_{Cl^-}	**3** (%)	**5** (%)
2.5 × 10^{-4}	S.a.[a]	0.080 ± 0.008	0.058 ± 0.004	16	38
5.0 × 10^{-4}	S.a.[a]	0.073 ± 0.007	0.056 ± 0.004	15	36
1.0 × 10^{-3}	S.a.[a]	0.080 ± 0.008	0.057 ± 0.004	10	32
2.5 × 10^{-4}	3.2	0.080 ± 0.008	N.t.[b]	24	16
2.5 × 10^{-4}	10.7	0.042 ± 0.004	N.t.[b]	12	46

[a] S.a.: slightly acidic. [b] N.t.: not titrated.

Photolysis in the presence of oxygen. In oxygen-saturated and acidic solutions, **8** is the main photoproduct, accounting for 42 to 60% of converted **1**. This result is in line with the detection of cyanobenzo-1,4-quinone-*O*-oxide in laser-flash photolysis experiments. Quantum yields of the photodegradation of **1** and chemical yields of **3**, **5**, **8** and of chloride ions in O_2-saturated solution are given in Table 2.

Photolysis in the presence of propan-2-ol. In the presence of propan-2-ol (0.13 M) and in the absence of oxygen, **1** is transformed into 2-hydroxybenzonitrile **9** with 95% yield. In solutions containing both oxygen and propan-2-ol, **8** and **9** are formed competitively (see Table 2): as the concentration of propan-2-ol is increased from 0.13 to 1.3 M, the chemical yield of **9** increases from 36 to 59% whereas that of **8** decreases from 36 to 8%.

In the presence of propan-2-ol and in the absence of oxygen, Φ_1 is equal to 0.063 ± 0.005 whereas it is only 0.035 ± 0.004 in oxygenated solution. This decrease in photodegradation yield in the presence of oxygen may be the result of a triplet quenching and therefore the indication that a triplet-state reaction is involved in the photoprocess.

Photolysis in ethanol. The irradiation of **1** in deoxygenated ethanol yields exclusively **9** with a quantum equal to 0.075 ± 0.008. In oxygen-saturated solution, the photolysis of **1** is negligible. The reaction is inhibited by one-half by acrylamide (6.3 × 10^{-3} M).

Involvement of the triplet state of 1 in aqueous solution. Experiments involving the heavy-atom intersystem crossing enhancers bromide and iodide ions which do not absorb at 313 nm, were undertaken in order to confirm the involvement of the triplet. The results are summarized in Table 3. Addition of bromide or iodide ions significantly enhances the photolysis quantum yield, Φ_1, the effect of iodide being more pronounced than that of bromide. These results can be interpreted in terms of a heavy-atom effect. Saturation with oxygen in the presence of iodide (0.48 M) again reduces Φ_1. In the presence of bromide or iodide ions, the reaction is very clean as far as products are concerned: bromo-2-hydroxybenzonitrile **10** was identified as the sole photoproduct in solutions containing bromide ions.

Upon addition of acrylamide (1.5 × 10^{-3} M) and in the absence of oxygen, the quantum yield of **1** disappearance is not affected, but the formation of **3** and **5** is drastically inhibited. These results confirm that acrylamide does not interact with the

Table 2 Photolysis of **1** in oxygen-saturated medium. Quantum yield of **1** photolysis (Φ_1), quantum yield of chloride ion formation (Φ_{Cl^-}) and chemical yields of photoproducts **3**, **5**, **8** and **9**

[**1**]/M	Conditions	Φ_1	Φ_{Cl^-}	**3** (%)	**5** (%)	**8** (%)	**9** (%)
2.5 × 10^{-4}	S.a.[a]	0.038 ± 0.004	0.038 ± 0.004	13	—	53	—
5.0 × 10^{-4}	S.a.[a]	0.037 ± 0.004	0.037 ± 0.004	11	—	54	—
1.0 × 10^{-3}	S.a.[a]	0.035 ± 0.004	0.031 ± 0.004	9	—	60	—
2.5 × 10^{-4}	pH = 3.2	0.031 ± 0.003	N.t.[b]	10	—	42	—
2.5 × 10^{-4}	pH = 10.7	0.02 ± 0.005	N.t.[b]	Traces	—	30	—
2.5 × 10^{-4}	S.a.,[a] propan-2-ol 0.13 M	0.030 ± 0.005	N.t.[b]	—	—	36	36
2.5 × 10^{-4}	S.a.,[a] propan-2-ol 0.39 M	0.041 ± 0.005	N.t.[b]	—	—	19	54
2.5 × 10^{-4}	S.a.,[a] propan-2-ol 0.65 M	0.055 ± 0.005	N.t.[b]	—	—	14	44
2.5 × 10^{-4}	S.a.,[a] propan-2-ol 1.3 M	0.053 ± 0.005	N.t.[b]	—	—	8	59

[a] S.a.: slightly acidic. [b] N.t.: not titrated.

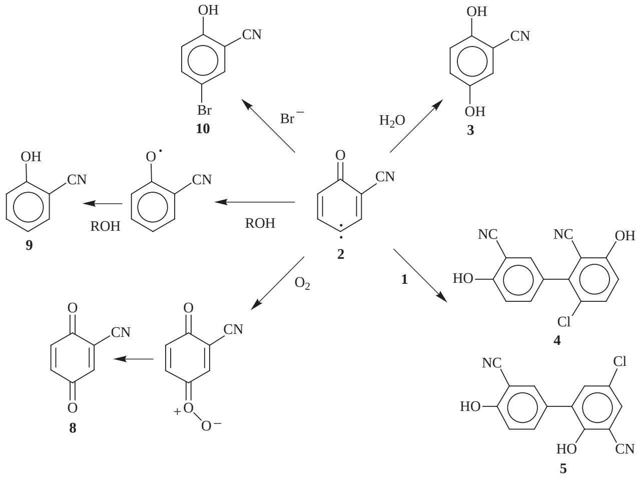
Table 3 Photolysis of deoxygenated and slightly acidic solutions of **1** (5.0×10^{-4} M) in the presence of acrylamide, bromide and iodide ions. Quantum yield of **1** photolysis (Φ_1) and chemical yields of photoproducts **3**, **5** and **10**

Additive	[Additive]/M	Φ_1	**3** (%)	**5** (%)	**10** (%)
No additive		0.073 ± 0.007	15	36	—
Acrylamide	1.5×10^{-3}	0.055 ± 0.005	2	5	—
Bromide ions	0.01	0.062	—	—	95
	0.1	0.051	—	—	95
	0.3	0.064	—	—	95
	0.82	0.11	—	—	95
	2.0	0.19	—	—	95
Iodide ions	0.01	0.060	—	—	—
	0.048	0.076	—	—	—
	0.48	0.20	—	—	—
Iodide ions, oxygen-saturated solution	0.48	0.085	—	—	—

triplet but with the carbene to yield new and non-identified photoproducts.

Discussion

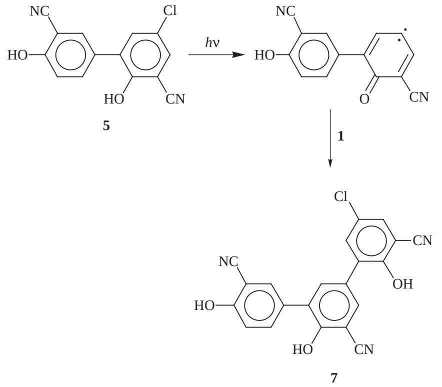
Transient absorption as well as product studies have demonstrated that the carbene, 3-cyano-4-oxocyclohexa-2,5-dienylidene **2**, is the key intermediate in the photolysis of **1**. This hitherto unknown carbene could be characterized by its UV absorption and by its characteristic reactions, addition of O_2 to give a cyanobenzoquinone-*O*-oxide and H-abstraction from propan-2-ol to give a 2-cyanophenoxyl radical. Its properties are thus similar to those of unsubstituted 4-oxocyclohexa-2,5-dienylidene resulting from photolysis of 4-chlorophenol;[3] in particular, its spectrum and reactivity indicate that it has a triplet ground state too. Unfortunately, the substrate solubility and low photoreaction quantum yield precluded a quantitative study of carbene reaction kinetics. However, the photoproduct studies are in complete agreement with the carbene hypothesis. All observed photoproducts can be traced to carbene reactions, as shown in Scheme 1.



Scheme 1 Reactivity of carbene **2**.

Comparison of the product distribution obtained in the present study with that from 4-chlorophenol[3] yields some interesting differences. The carbene **2** has a distinctly lower tendency to give the photohydrolytic product: at 2.5×10^{-4} M, 4-chlorophenol yielded about 45% of hydroquinone,[3] whereas **1** produces only 16% of **3**. Substitution of the carbene by the CN group thus favors the coupling reactions. On the other hand, competition between the yields of **3** and **5** is not clear-cut. This points to a more complex reaction mechanism in comparison to that of 4-chlorophenol. It is conceivable that CN substitution destabilizes at least some of the possible products of addition of the carbene on **1**, thereby promoting their dissociation into radicals. The presence of the non-halogen-containing cyanohydroxybiphenyl **6** may be taken as an indication of such a process.

Secondary photolytic transformations of the coupling products are observed in moderately concentrated solution of **1**. The presence of the terphenyl **7** among the products could be analytically demonstrated; its formation can be explained by the secondary photolysis of **5** (Scheme 2).



Scheme 2 Mechanism of **7** formation.

From the point of view of the overall quantum yield, the CN-substituted derivative is much less photoreactive than 4-chlorophenol. By taking Φ_1 values measured in the presence of propan-2-ol or bromide ions (10^{-2} M), *i.e.* in conditions where carbene **2** is fully trapped, we can estimate the quantum yield of **2** formation as 0.062. In the case of 4-chlorophenol, the quantum yield of carbene formation was 0.75, *i.e.* more than ten times higher.[3] This difference points to limiting processes on the time scale of the primary photoinitiated steps, since the substrate can hardly be regenerated once dehalogenation has taken place.

Transient absorption spectroscopy has demonstrated that photoionization of **1**, both monophotonic and biphotonic, contributes to photolysis on the nanosecond–microsecond time scale, in contrast to 4-chlorophenol,[3] where it could be detected in alkaline medium only. This is the consequence of the high excited-state acidity of **1** brought about by CN substitution. However, the products determined in conditions of continuous irradiation bear no trace of this pathway. This observation may be explained by lack of reactivity of the radicals produced in the photoionization step, in line with the generally low reactivity of phenoxyl radicals[20] on the one hand and with the low dehalogenation tendency of *m*-chlorobenzonitrile radical anions[17] on the other; if so, geminate radicals would have a high tendency towards in-cage recombination. Photoionization thus conceivably contributes little to the phototransformation of **1**, and the overall quantum yield is correspondingly reduced.

Other (and quantitatively speaking more relevant) processes limiting the phototransformation yield may be of a photophysical nature. In this connection, it is important to consider the fact that the carbene **2** (as well as the carbene resulting from 4-chlorophenol dehalogenation) has a triplet ground state. An intersystem crossing step must therefore come into play at some stage of the photoprocess. With the 4-halogenophenols, it was until now not possible to decide whether this step occurs at the substrate molecule level or at the carbene level. In this respect, CN substitution has turned out to be a valuable tool by enabling triplet quenching as well as heavy atom effects on the photoproduct yields.

The study of the photoinduced reactions of **1** in ethanolic solution, both by transient spectroscopy and product analysis, gave clear evidence in support of the assumption that intersystem crossing on the molecular level precedes dehalogenation. The study of transients and photoproducts confirmed that the photoreaction mechanism is the same in aqueous and in ethanolic solution. The triplet–triplet absorption of **1** was easily measurable in this latter solvent. Triplet quenching by O_2 dramatically reduced the formation of the transients generated by carbene trapping on the one hand, and the degradation of **1** following continuous irradiation on the other. A detailed examination of the laser-induced transients in deoxygenated ethanolic solution showed that H atom abstraction from the alcohol by the carbene is not a very fast process and may be rate-determined by triplet decay. The study of the influence of acrylamide on triplet decay and 2-cyanophenoxyl formation led to the same conclusion. It has to be noted that the triplet quantum yield measured by energy transfer to anthracene is much higher than the quantum yield of phototransformation; the latter contributes only about 12% to overall triplet decay.

The second evidence for involvement of the molecular triplet came from the experiments using bromide or iodide as heavy-atom enhancers of intersystem crossing in aqueous solution. The results clearly show that the phototransformation yield is enhanced by addition of the halides, in a manner consistent with the heavy-atom effect. This means that in aqueous solution the triplet yield must be relatively low in the first place; this again constitutes a difference with respect to the 4-chlorophenol case, where bromide addition changed the product distribution (in the same way as with **1**, *i.e.*, towards a clean substitution of Cl by Br) but not the photoreaction yield.[3] The reason for this difference probably lies in the fact that in the case of **1** intersystem crossing has to compete with excited-state deprotonation, thereby lowering the triplet yield. In the anionic form of the phenol, the triplet yield is inherently lower; this is shown by the lower photoreaction yields obtained in alkaline solution from **1** as well as from 4-chlorophenol.[3]

In contrast to the ethanolic solution, a time-resolved study of the triplet state could not be conducted in aqueous solution on account of its shorter lifetime (τ/ns < 100) and lower yield. Indeed, triplet quenching by O_2 in water is only partial, thus allowing observation of cyanobenzo-1,4-quinone-*O*-oxide production, which is not seen in ethanol; in the case of acrylamide interaction with the triplet is even minor, while the majority of product quenching probably involves an interaction with the carbene. Nevertheless, compared to 4-chlorophenol the effect of CN substitution is clearly that of a lengthening of the triplet lifetime; in the former case[3] there was no detectable influence of O_2 on the yield of phototransformation.

Conclusions

This study shows that the carbene 3-cyano-4-oxocyclohexa-2,5-dienylidene is the key intermediate in the photolysis of **1**. This transient is converted into substrate addition products (substituted biphenyls), cyanobenzo-1,4-quinone-*O*-oxide or 2-hydroxybenzonitrile by reaction with **1**, oxygen or propan-2-ol, respectively.

The substitution of 4-chlorophenol by the CN group in the *ortho* position to the hydroxy group has the double consequence of lowering the triplet yield of the neutral molecule, due to fast deprotonation of the excited singlet in competition with intersystem crossing, and of increasing the triplet lifetime. Both effects could be exploited to show that the photochemistry of **1** involves the triplet state of the molecule, and thus provide evidence in support of the assumption that the intersystem crossing step on the way to the triplet ground state of the carbene takes place on the molecular and not on the carbene level. Additionally, excited-state deprotonation entails formation of hydrated electrons from the singlet excited state of the anion, but this process does not affect the photochemistry in a detectable way.

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