Study of the aqueous photochemistry of 4-fluorophenol, 4-bromophenol and 4-iodophenol by steady state and nanosecond laser flash photolysis

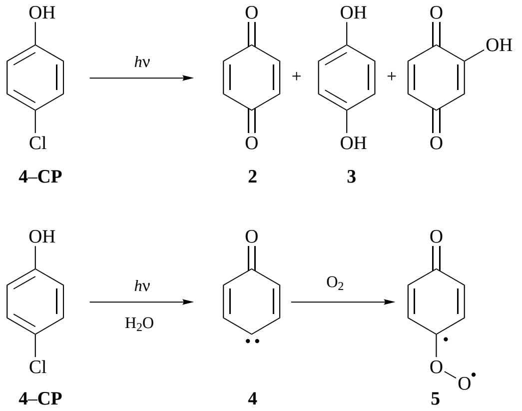
Anne-Pascale Durand,[a] Robert G. Brown,*[a] David Worrall[b] and Francis Wilkinson[b]

[a] *Chemistry Dept., University of Central Lancashire, Preston, UK PR1 2HE*
[b] *Chemistry Dept., Loughborough University of Technology, Loughborough, UK LE11 3TU*

The mechanisms of the aqueous photoreactions of 4-fluorophenol, 4-bromophenol and 4-iodophenol have been studied by steady state photolysis and by nanosecond laser flash photolysis. The same photoproducts are obtained as were found in the photolysis of aqueous 4-chlorophenol although the photoreaction quantum yields vary considerably across the series of compounds. As for 4-chlorophenol the carbene 4-oxocyclohexa-2,5-dienylidene is formed from the halogenophenol by loss of HX and this species reacts efficiently with oxygen to form 1,4-benzoquinone *O*-oxide which subsequently yields 1,4-benzoquinone. Consideration of the reaction quantum yields together with the photophysical properties of the four halogenophenols suggests that the carbene is derived from the first excited singlet state rather than a triplet excited state.

The photochemistry of 4-chlorophenol (4-CP, **1**) in aqueous solution is currently enjoying a surge of interest due to its use as a model compound for the aqueous photochemistry of chlorinated aromatics and for assessing the effectiveness of advanced oxidation methods.[1–4] In aqueous solution 4-CP undergoes a range of photochemical reactions depending on the presence of oxygen, the concentration of the chlorophenol and the pH. At neutral or acidic pH values, where the 4-CP is not ionised, and in the presence of oxygen, the principal photoproduct is 1,4-benzoquinone **2**.[5–8] A range of minor products are also observed, including 1,4-hydroquinone **3**, 2-hydroxy-1,4-benzoquinone and several polyhydroxybiphenyls,[5,7] the latter becoming particularly prevalent when the solution is oxygen free. There has been some controversy as to whether 1,4-benzoquinone is a photoproduct in the absence of oxygen but it is now clear that it is not[7,9] and that earlier work which suggested the opposite[6,8] was in error due to insufficiently rigorous degassing of the solutions.

The mechanism of 4-CP photolysis in water has very recently been shown to involve the formation of, firstly, 4-oxocyclohexa-2,5-dienylidene **4**, followed by 1,4-benzoquinone *O*-oxide **5** if molecular oxygen is present (Scheme 1).[10,11] These two radical species are readily observable by nanosecond flash photolysis.



Scheme 1 Photoproducts and mechanism for the photoreaction of 4-chlorophenol in neutral, aerated aqueous solution at ambient temperature

By contrast, the aqueous photochemistry of the other 4-halogenophenols has been almost completely neglected. Lipczynska-Kochany[12] has determined the photoproducts from aqueous 4-bromophenol (4-BP, **6**) to be 1,4-benzoquinone (major product) and 1,4-hydroquinone (minor product) together with small amounts of 2-hydroxy-1,4-benzoquinone **7** which is a known photoproduct of **2** and almost certainly arises from secondary photolysis. This product mix is very similar to that observed from 4-chlorophenol[5–8] and Grabner *et al.* also report that aqueous 4-bromophenol gives a similar distribution of photoproducts to 4-chlorophenol.[10] Further work on 4-BP by Lipczynska-Kochany and Kochany[13] using EPR with a spin trap yielded four possible radical intermediates; namely an aryl radical (possibly a 4-hydroxyphenyl radical), hydrated electrons, hydroxy radicals and the *para*-benzosemiquinone anion. Again, these findings are in line with similar experiments on 4-chlorophenol.[14] However, they are clearly at odds with the flash photolysis results[10,11] and the similarity of the products for **1** and **6** would suggest that the photolysis mechanisms for the two compounds are very similar.

We have undertaken a fairly comprehensive study of the aqueous photochemistry of 4-chlorophenol.[8,9,11] In order to gain further insight into the aqueous photochemistry of this class of compounds we have also undertaken experiments on the other three commonly available 4-halogenophenols.[15] These experiments appear to both confirm that the mechanistic details for **1** apply across the other 4-halogenophenols and provide insight into the reactive excited state. We report the results of those experiments here.

Experimental

4-Chlorophenol was obtained from Aldrich Chemicals Ltd and was sublimed (40–45 °C, 11 mbar) before use. 1,4-Benzoquinone, 4-bromophenol, 4-iodophenol and 1,10-phenanthroline were obtained from Lancaster Synthesis Ltd. 1,4-Hydroquinone, 4-fluorophenol and the four 4-halogenoanisoles were obtained from BDH Ltd. Water was distilled and deionised and absolute ethanol was Burroughs AR reagent grade.

An Applied Photophysics Ltd. KR2 microsecond flash spectrometer was used to photolyse the samples contained in cylindrical quartz cuvettes of 10 cm length and 2 cm diameter.

Table 1 Absorption and emission properties of the 4-halogenophenols and 4-halogenoanisoles in water and ethanol[a]

		Absorption		Fluorescence		
Compound	Solvent	λ_{max}/nm	ε/dm^3 mol^{-1} s^{-1}	λ_{max}/nm	φ_f	τ_f/ns
4-FP	Water	278	2230	310	0.144	2.1
4-CP	Water	280	1400	312	0.015	0.4
4-BP	Water	280	1370	310	0.0004	<0.1
4-IP	Water	280	1250	—	<0.0001	—
4-FP	Ethanol	282	2450	310	0.162	1.5
4-CP	Ethanol	282	1770	310	0.048	0.4
4-BP	Ethanol	282	1600	307	0.002	<0.1
4-IP	Ethanol	282	1490	—	<0.0001	—
4-FA	Ethanol	280	2280	306	0.166	2.0
4-CA	Ethanol	280	1700	308	0.023	0.5
4-BA	Ethanol	280	1500	308	0.0004	<0.1
4-IA	Ethanol	280	1340	—	<0.0001	—

[a] The three iodo compounds were non-fluorescent under the instrumental conditions used here. Fluorescence quantum yields are ±10% and lifetimes ±0.2 ns.

Flash energies of approximately 50 J were used with a flash duration of approximately 25 μs FWHM. Product analysis was carried out by HPLC with a Perkin-Elmer Series 10 LC pump, guard column and a Pecosphere-3*3C-C18 column, a Perkin-Elmer LC-235 UV detector and a Perkin-Elmer model 1020 integrator. The detection wavelength was 280 nm. The mobile phase used was acetonitrile–water (20:80) acidified to pH 4.5 with orthophosphoric acid. A flow rate of 2 cm^3 min^{-1} was chosen. Steady state photolyses were also carried out in a Photochemical Reactors Ltd. model MLU18 photoreactor. Quantum yields of photoreaction were determined using this system together with ferrioxalate actinometry.[16]

Absorption spectra were recorded on a Hewlett-Packard model 8452A diode-array spectrometer. Fluorescence spectra were measured using a Spex Fluoromax spectrofluorimeter. Fluorescence decay profiles were measured by the time-correlated single photon counting technique[17] at the EPSRC Daresbury Laboratory. The equipment used at Daresbury has been described elsewhere.[18] The decay profiles were analysed by computer convolution and were uniformly found to be single exponential decays on the basis of the calculated χ^2 value and the distribution of residuals.

Nanosecond flash photolysis was carried out with an HY200 Nd: YAG laser (Lumonics) at an excitation wavelength of 266 nm. The full instrumentation is described elsewhere.[11] A concentration of approximately 1.0×10^{-3} mol dm^{-3} was used for the majority of the measurements. This gives an absorbance at 266 nm of approximately 0.4. Samples were only subjected to a single flash before they were replaced by a fresh solution.

Results

Absorption and emission properties of the four 4-halogenophenols in solution at ambient temperature

The absorption and emission properties of the four 4-halogenophenols (4-FP to 4-IP) were measured in aqueous and ethanolic solution and are presented in Table 1 alongside the corresponding data for the four 4-halogenoanisoles (4-FA to 4-IA). It can be seen that the absorption and emission maxima are almost completely independent of molecular structure and solvent. In addition, the other properties given in Table 1 are also relatively independent of the other variables (*i.e.* solvent and the hydroxy/methoxy group) for a given halogen.

The extinction coefficients exhibit a significant decrease with increasing atomic number of the halogen in both solvents, presumably reflecting the decreasing electron-withdrawing power of the halogen as it gets heavier. The fluorescence quantum yield and lifetime data when taken together show, as might be expected, a clear heavy atom effect. Calculation of radiative rate constants (k_f) and rate constants for the sum of the non-emission processes reveals clear increases in the latter with the increasing atomic number of the halogen for all three series of compound/solvent. These data have to be interpreted with some caution given that a substantial contribution to this 'non-radiative' rate constant arises from ring-halogen bond scission leading to the observed photoproducts. However, as discussed later, even when this is taken into account a substantial heavy atom effect remains, implicating the singlet state. On the basis of the k_f values, we can estimate that the fluorescence lifetime of 4-BP is of the order of 10 ps and for 4-IP much less than this.

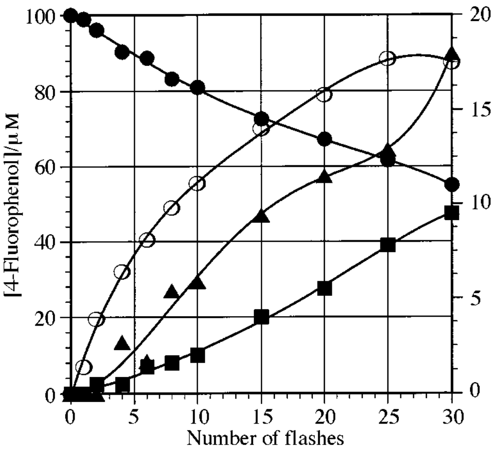


Fig. 1 Variation of the concentration of 4-fluorophenol (●), 1,4-benzoquinone (○), 1,4-hydroquinone (■) and the material unaccounted for (▲) as a function of flash number in the photolysis of aerated aqueous 4-fluorophenol (100 μM)

Photolysis of aerated aqueous 4-fluorophenol, 4-bromophenol and 4-iodophenol

Photolysis of aerated aqueous 4-FP, 4-BP and 4-IP was carried out under the same experimental conditions as used for the aqueous photolysis of 4-CP.[8,9] In the case of 4-FP, the first (and major) photoproduct identified was 1,4-benzoquinone. This appeared immediately in the photolysis (whose time course is shown in Fig. 1) and was followed by the appearance of 1,4-hydroquinone and 2-hydroxy-1,4-benzoquinone at later stages of the photolysis. A fourth, as yet unidentified photoproduct, was also obtained which is not present in the photolysis products of any of the other 4-halogenophenols. We are currently trying to identify this photoproduct using LC/MS as previously.[9] For the first few flashes, the amount of 4-FP that had photoreacted was entirely accounted for by the 1,4-benzoquinone formed. After further photolysis, the majority of the consumed 4-FP is accounted for by the 1,4-benzo-

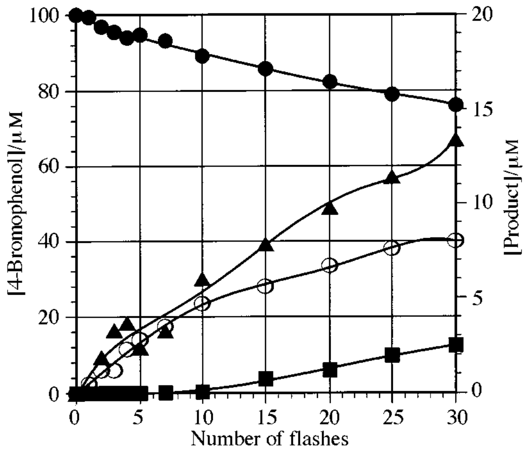


Fig. 2 Variation of the concentration of 4-bromophenol (●), 1,4-benzoquinone (○), 1,4-hydroquinone (■) and the material unaccounted for (▲) as a function of flash number in the photolysis of aerated aqueous 4-bromophenol (100 μM)

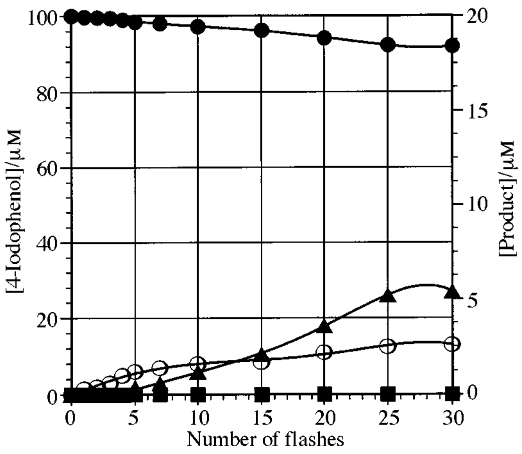


Fig. 3 Variation of the concentration of 4-iodophenol (●), 1,4-benzoquinone (○), 1,4-hydroquinone (■) and the material unaccounted for (▲) as a function of flash number in the photolysis of aerated aqueous 4-iodophenol (100 μM)

quinone and 1,4-hydroquinone photoproducts but by the end of the photolysis, there is a significant amount of material unaccounted for as shown in Fig. 1.

1,4-Benzoquinone and 1,4-hydroquinone were also identified as photoproducts of 4-BP photolysis whose time course is shown in Fig. 2. 2-Hydroxy-1,4-benzoquinone was not identified among the photoproducts although it was detected by Lipczynska-Kochany.[12] This is almost certainly because the amount of 4-BP photolysed is much less than for 4-FP and 4-CP so that the concentration of the 1,4-benzoquinone, which is the precursor of 2-hydroxy-1,4-benzoquinone, is much lower than for the other compounds. Photolysis of aqueous 4-IP (Fig. 3) yielded 1,4-benzoquinone as the only detectable and confirmed photoproduct. The photolysis rate for 4-IP was once again greatly reduced compared even to 4-BP. As with 4-FP and 4-CP, the amount of material unaccounted for in the identified photoproducts steadily builds up during the photolyses of both 4-BP and 4-IP.

Based on the amount of the halogenophenol remaining at the end of thirty flashes, the reactivity of the four compounds is 4-CP > 4-FP > 4-BP > 4-IP, and this is reflected in the quantum yields for the consumption of the halogenophenol which were found to be 0.31, 0.44, 0.08 and 0.022 for 4-FP, 4-CP, 4-BP and 4-IP, respectively. These quantum yields were determined by ferrioxalate actinometry based on photolysis of $\leq$10% of the initial halogenophenol concentration.

We conclude that there are two competing effects which determine the reaction quantum yield; the strength of the bond between the halogen and the aromatic ring and a heavy atom effect on the rate of non-radiative decay. The former acts to increase the quantum yield with increasing atomic weight whereas the latter works in the opposite direction. It appears from the quantum yield data that the heavy atom effect is the more dominant of the two.

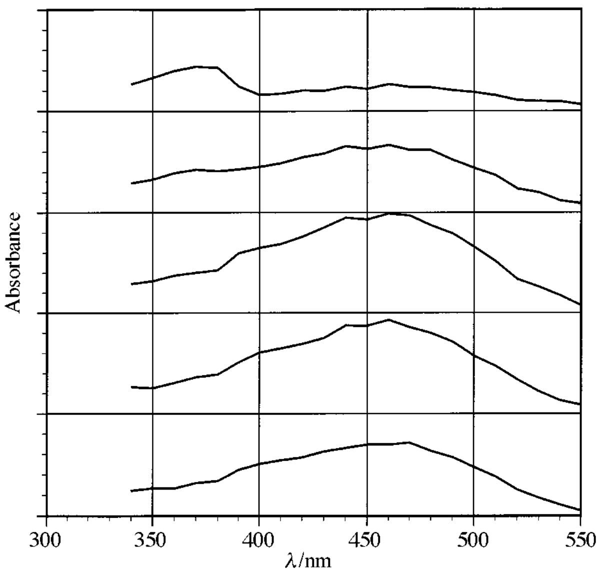


Fig. 4 Transient absorption spectra for 4-fluorophenol (1.0 mM) in aerated water at delay times of 0.21 μs (top spectrum), 0.88, 2.48, 5.59 and 9.27 μs (bottom spectrum). Absorbance range for each spectrum 0–0.1.

Nanosecond flash photolysis of 4-fluoro-, 4-bromo- and 4-iodophenol in aerated aqueous solution

Aqueous solutions of 4-FP, 4-BP and 4-IP were subjected to nanosecond laser flash photolysis for comparison with 4-chlorophenol. 4-Fluorophenol gives virtually identical results to 4-chlorophenol. The transient spectra which are obtained from a typical set of experiments are shown in Fig. 4. Comparison with the corresponding data for 4-CP[11] shows that these spectra are very similar to those for 4-CP in both their shape and overall intensity. We therefore conclude that the same two transient species are formed in both cases with approximately the same yields. Analysis of the individual kinetic traces gave, as expected on the basis of this conclusion, very similar results to those found for 4-chlorophenol. Above 400 nm the traces were adequately fitted (see Fig. 5) by eqn. (1), with

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

$A_1 = -A_2$, $k_1 = 0.95 \pm 0.10 \times 10^6\ \text{s}^{-1}$ (compared with $1.0 \pm 0.1 \times 10^6\ \text{s}^{-1}$ for 4-CP) and $k_2 = 6.7 \pm 1.0 \times 10^4\ \text{s}^{-1}$ (compared with $8.5 \pm 1.0 \times 10^4\ \text{s}^{-1}$ for 4-CP). The slight difference in the values of k_1 and k_2 for 4-fluoro- and 4-chloro-phenol are not considered to be significant.

Below 400 nm, where both transients absorb, the traces are less easy to analyse. At some wavelengths, the observed absorption changes can be fitted with a single exponential decay plus a constant term whereas data at other wavelengths require the double exponential form of eqn. (1) (but with $A_1 \neq -A_2$ and $|A_1| < |A_2|$) to achieve an acceptable fit. The relative weakness of the transient signals below 400 nm means that we have less confidence in the fitted parameters than at the higher wavelengths but similar rate constant values to those given above are observed at the shorter wavelengths. This supports the suggestion of an initially formed transient which absorbs below 400 nm and which decays to form a second transient, which then itself decays *i.e.* there is a clear parent–daughter relationship

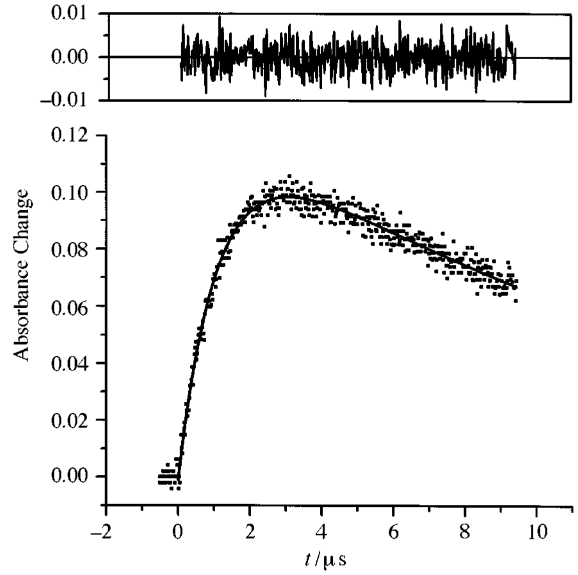


Fig. 5 Transient absorption of 4-fluorophenol (1.0 mM) in aerated aqueous solution monitored at 470 nm, together with biexponential fitted curve and residuals

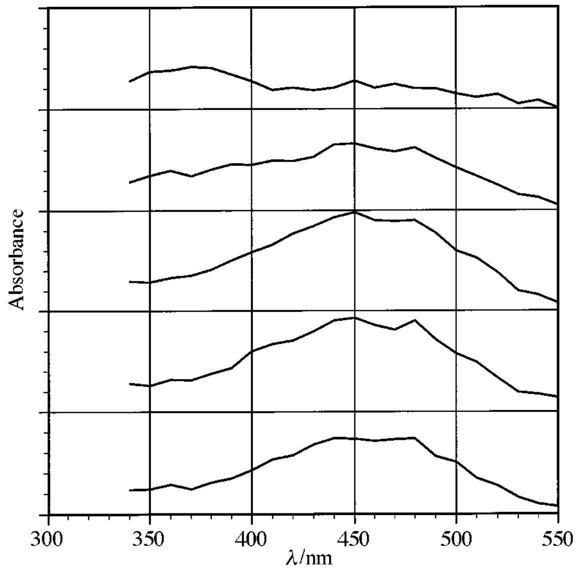


Fig. 6 Transient absorption spectra for 4-bromophenol (1.0 mM) in aerated water at delay times of 0.21 μs (top spectrum), 0.88, 2.48, 5.59 and 9.23 μs (bottom spectrum). Absorbance range for each spectrum 0–0.05.

between the two transients. Thus below 400 nm the kinetic traces are a combination of the decay of the first transient species together with the rise and subsequent decay of the second transient.

In the case of 4-bromophenol, transient spectra were obtained which were the same shape as for the previous two halogenophenols (Fig. 6) but which were of reduced intensity. It appears that the same transients are being produced as for 4-FP and 4-CP but with lower yields. Analysis of the kinetic traces above 400 nm on the basis of eqn. (1) gave $A_1 = -A_2$, $k_1 = 0.94 \pm 0.10 \times 10^6$ and $k_2 = 5.2 \pm 1.0 \times 10^4\ s^{-1}$. Fig. 7 shows an example of one of these analyses. Once again the traces at wavelengths less than 400 nm are more difficult to analyse, partly as a result of the reduced intensity of the transients and partly because of the presence of the same two overlapping bands as above. However, identical comments about these kinetic traces for 4-BP may be made as for the corresponding profiles for 4-FP.

Finally, a 10^{-3} mol dm^{-3} aqueous solution of 4-iodophenol

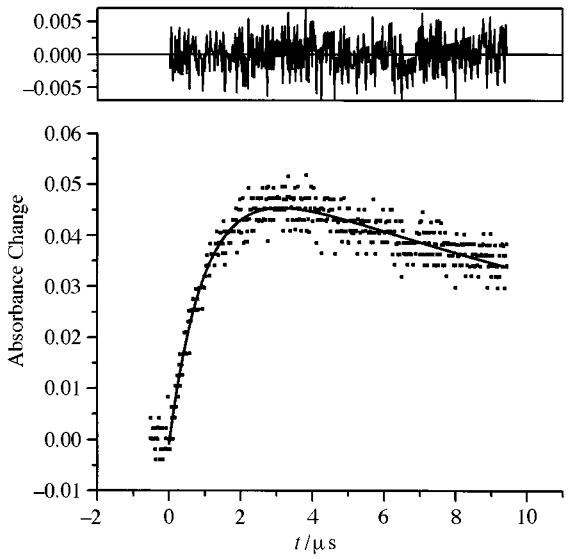


Fig. 7 Transient absorption of 4-bromophenol (1.0 mM) in aerated aqueous solution monitored at 470 nm, together with biexponential fitted curve and residuals

was flashed under identical conditions. Little or no transient absorption was obtained and this was also the result for oxygen-saturated and freeze–thaw degassed samples.

Discussion

All four 4-halogenophenols appear to exhibit very similar photochemistry in aerated aqueous solution in terms of the nature of the photoproducts obtained under steady-state photolysis as well as the nature of the transient species observed following nanosecond flash excitation (excluding 4-IP where any transient absorption was too weak to detect). Comparison of the four compounds at a similar stage of photolysis reveals very clearly the similarities between the compounds in terms of the photoproducts but also particularly highlights the effect of prolonged photolysis. For 4-CP, the most reactive of the four, a single flash is sufficient to destroy approximately 10% of the compound[8] and this loss is almost entirely accounted for by the two main photoproducts (1,4-benzoquinone and 1,4-hydroquinone); there is only a small amount of material unaccounted for.

For the less reactive compounds, a higher and higher number of flashes is required to achieve the same level of conversion of the starting material and it is noticeable that the yields of the two main photoproducts decrease with increasing flash number due to their participation in secondary photochemistry. This is also evidenced by the increasing amount of material which is unaccounted for by these two main photoproducts. The most extreme case is 4-IP where only about one third of the iodophenol which has been destroyed after 30 flashes is accounted for in the main photoproducts; two thirds of the photolysed material is present as secondary photoproducts of various kinds. These observations are in complete agreement with the quantum yields for the disappearance of the halogenophenol and the yield of transient species during nanosecond laser flash photolysis of the four compounds.

The observation of identical initial photoproducts and transients during the flash experiments (both albeit with different yields for the different compounds) would suggest that the photochemistry of 4-FP, 4-BP and 4-IP in aerated, aqueous solution follows the same path as 4-CP in that loss of HX leads to the formation of 4-oxocyclohexa-2,5-dienylidene **4** followed by 1,4-benzoquinone *O*-oxide **5** as shown in Scheme 1. These assignments appear to be at odds with the transient species detected by spin-trapping–EPR.[13,14] However, it is possible that the 'aryl radical' detected by Lipczynska-Kochany and

Kochany in the photolysis of 4-CP and 4-BP could be the carbene 4-oxacyclohexa-2,5-dienylidene and that 1,4-benzoquinone *O*-oxide could be confused with a semiquinone species when spin-trapped. Alternatively, the semiquinone anion detected in the EPR experiments could result from secondary photochemistry of the 1,4-benzoquinone photoproduct.

The nature of the excited state which leads to carbene **4** (which is known to have a triplet ground state[19]) is open to speculation. It is possible to envisage two main routes following excitation of the ground state halogenophenol. These differ depending on whether loss of HX takes place from the halogenophenol triplet state following intersystem crossing (ISC) or whether it takes place from the initially excited halogenophenol singlet state and the singlet carbene thus produced then intersystem crosses to its triplet ground state.

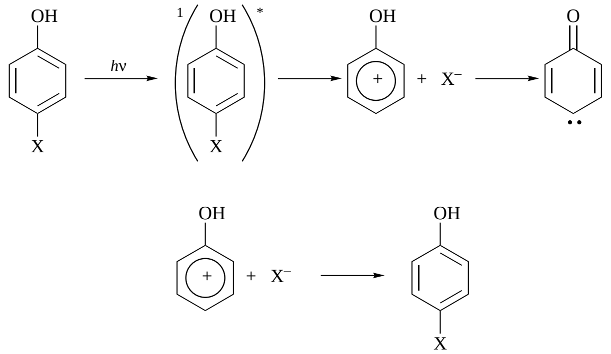
The evidence available to help differentiate between these two possibilities consists of the effects of changing the halogen atom and the effect of oxygen on the yield of carbene. We have previously found that the yield of **4** in the photolysis of aqueous 4-CP is approximately the same in aerated and degassed solution and is perhaps slightly higher in oxygen-saturated solution.[11] Since oxygen is a well-known triplet quencher these observations would tend to imply that the chlorophenol triplet state is not involved in the photochemical pathway to **4** and we have not observed any transient which we can assign to a triplet state of any of the four halogenophenols. However, oxygen is not as soluble in water as in other solvents so that this, together with a short-lived triplet state, could account for the similar carbene yields in aerated, oxygenated and degassed water. The effect of oxygen is inconclusive with respect to determining the early mechanistic details.

Changing the halogen atom in the halogenophenol will have several effects. Firstly, the C–X bond strength decreases from fluorine through to iodine[20] making bond cleavage easier and potentially increasing the yield of **4**. Secondly, the heavy atom effect will operate and catalyse any ISC processes in the halogenophenols. If loss of HX occurs from the excited singlet state, ISC will compete with this and we would anticipate decreases in the fluorescence quantum yield and lifetime and the yield of **4** (and subsequent photoproducts) as the lighter halogens are replaced by the heavier. The effect of the halogen substituent on the fluorescence properties of both the 4-halogenophenols and the 4-halogenoanisoles, where the quantum yield and lifetime decrease considerably as the atomic weight of the halogen increases (Table 1) is clearly in accord with the photoreaction originating in the excited singlet state. In addition we note that the photoreaction quantum yield and yield of **4** both decrease as the halogen substituent in the 4-halogenophenol is changed from fluorine to iodine. This is entirely consistent with reaction from the halogenophenol excited singlet state competing with ISC.

If loss of HX occurs from the halogenophenol triplet state the heavy atom effect would be expected to operate to enhance both $S_1 \longrightarrow T_1$ and $T_1 \longrightarrow S_0$ ISC. The first of these processes would again decrease the fluorescence yield and lifetime but would now enhance the yield of **4** whereas the second ISC process would act to decrease it. We were unable to detect a transient in our flash photolysis studies which could be attributed to a triplet state and must therefore conclude that it is formed in low yields or is short-lived (lifetime <100 ns) or both. This means that we are unable to quantify the effect of the halogens on the $T_1 \longrightarrow S_0$ ISC. However, if the photoreaction does originate from the excited triplet state, our failure to detect it due to its short lifetime leads to the conclusion that the heavy atom effect on its lifetime will be small. The observed variation in the photoreaction yields is not consistent with this scenario.

In addition, the photoreaction quantum yield of 0.31 for 4-FP indicates that if reaction occurs from the triplet state, $S_1 \longrightarrow T_1$ ISC is already efficient and has a rate constant of *ca.* $1.5–4.0 \times 10^8$ s^{-1} (based on a minimum intersystem crossing yield of 0.31 and a maximum of 0.85). A similar calculation for 4-CP yields a range of rate constants of $1.0–2.5 \times 10^9$ s^{-1}. The lack of fluorescence lifetime data for the bromo and iodo compounds precludes analogous calculations for them but we note that for 4-FP and 4-CP the increase in the $S_1 \longrightarrow T_1$ ISC rate constant is considerably smaller than that calculated for 1-fluoro- and 1-chloro-naphthalene (where an increase of a factor of 100 in this ISC rate constant is found) which form part of the 1-fluoronaphthalene to 1-iodonaphthalene series analysed by Birks.[21] In this series, the heavy atom effect is rather greater on the $S_1 \longrightarrow T_1$ ISC process than on that for $T_1 \longrightarrow S_0$. If the same is true in the case of the 4-halogenophenols, then reaction from the excited triplet state is again precluded on the basis of our experimental data.

We therefore conclude that the mechanism for the formation of carbene **4** in the photolysis of the 4-halogenophenols in neutral aqueous solution is that given in Scheme 2. We have attempted to prove this mechanism by investigating the effect of an external heavy atom on the fluorescence properties and nanosecond flash photolysis of the 4-halogenophenols. We are not able to use bromide or iodide ions to undertake such experiments since these two ions would interfere in the reaction mechanism (see below), so we therefore chose ethyl iodide and xenon as possible external heavy atom quenchers. Unfortunately, both of these materials are insufficiently soluble in water to produce a significant quenching effect due to the relatively short singlet lifetimes of all four halogenophenols. In addition, the absorption spectrum of ethyl iodide overlaps that of the phenols. We have therefore been unable to validate our proposed mechanism by using such experiments.



Scheme 2 Mechanism for the formation of 4-oxocyclohexa-2,5-dienylidene in the photoreaction of the four halogenophenols in aerated aqueous solution at ambient temperature

The reaction quantum yields reported earlier represent a minimum yield for the formation of the carbene since recombination of the initial hydroxyphenyl cation–halide ion pair may occur before the cation loses a proton to form the carbene and Grabner *et al.*[10] report a quantum yield for the formation of **4** from 4-CP of 0.75. They also found that the decay rate of the carbene was enhanced in the presence of added halide ions with iodide ions being the most effective and concluded that the halide ion added directly to the carbene; this route would also decrease the yield of photodegradation if the halide ion adding to the carbene was the same as that in the original halogenophenol.

The initial heterolysis of the aryl–halogen bond has parallels in the photochemistry of fluoromethoxybenzenes in aqueous solution reported by Zhang and Wan.[22] Here HF was generated by substitution of the fluoride by water with initial loss of fluoride ion and the generation of an aryl cation. However it is interesting to note that a chloromethoxybenzene was felt to exhibit behaviour best explained by initial homolysis of the aryl–halogen bond rather than the heterolytic behaviour seen here for 4-CP and the other halogenophenols. It would be interesting to undertake faster flash experiments to try to observe these earlier transients which are postulated for these various reactions.

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