

Mechanism of 2-iodophenol photolysis in aqueous solution

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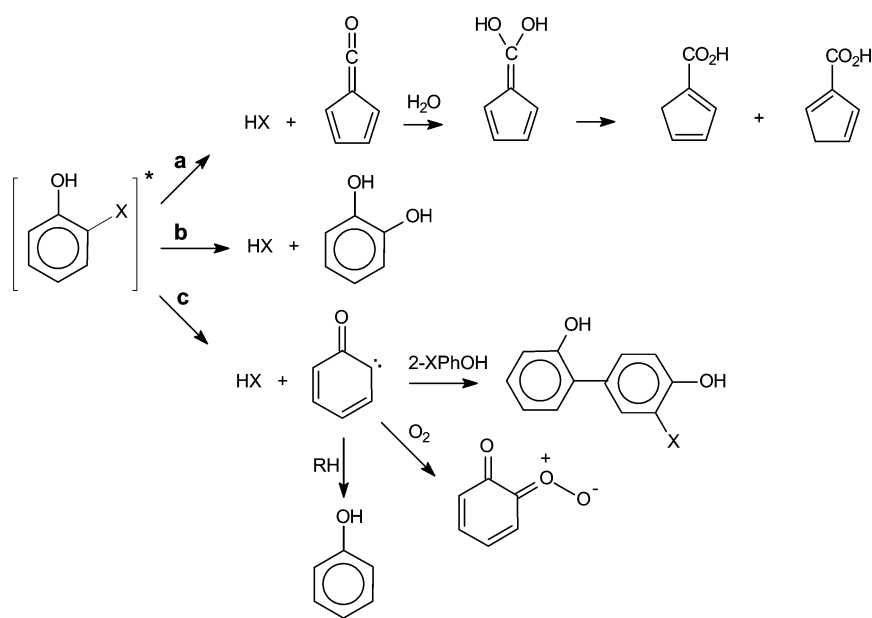
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The photolysis of 2-iodophenol (2-IPhOH) was investigated by means of laser flash photolysis and product studies. Two major heterolytic dehalogenation pathways could be evidenced upon irradiation of anionic 2-IPhO[−]: ring contraction leading to cyclopentadienic acids *via* a Wolff rearrangement ($\phi_a = 0.11 \pm 0.02$), and α -ketocarbene formation ($\phi_c = 0.03 \pm 0.01$) yielding products characteristic for triplet carbene reactivity. In contrast, the irradiation of neutral 2-IPhOH leads mainly to homolytic cleavage of the carbon-halogen bond ($\phi = 0.08 \pm 0.01$) with subsequent formation of biphenyls in deoxygenated solution. This specific reaction, which is not observed with other halogenated phenols, is explained by the low energy of the C–I bond. The relative efficiencies of the heterolytic pathways in the halogenophenol series are discussed in terms of the multiplicity of the excited states involved and of the internal heavy atom effect.

Introduction

The aqueous photochemistry of the *ortho*-halophenols, 2-chlorophenol (2-ClPhOH) and 2-bromophenol (2-BrPhOH), shows a complex and interesting behaviour. Previous investigations^{1–6} have demonstrated that three characteristic reactions occur subsequently to photoinduced heterolytic dehalogenation: (a) ring contraction yielding cyclopentadienic acids, (b) photohydrolysis into pyrocatechol, and (c) α -ketocarbene formation giving rise to biphenyls in deoxygenated solution (see Scheme 1).

Photocontraction (pathway a) was identified twenty years ago by Guyon and coworkers^{1,2} by means of photoproduct analysis. It is observed both for the neutral and the anionic forms of the halogenophenols ($pK_a \approx 8.5^{2,5}$), but is more efficient from the anion ($\phi_a = 0.30 \pm 0.03^1$ and 0.27 ± 0.03^3 for 2-ClPhO[−] and 2-BrPhO[−], respectively) than from the molecular form ($\phi_a = 0.042 \pm 0.008$ and 0.035 ± 0.007 for 2-ClPhOH and 2-BrPhOH, respectively⁴). Two transient intermediates involved in this pathway were detected by laser flash photolysis: cyclopenta-2,4-dienyl ketene ($\lambda_{max} = 255$ nm) and fulvene-6,6-diol ($\lambda_{max} = 295$ nm in acidic or neutral medium and



Scheme 1

283 nm at pH = 12), the latter being produced by addition of water on the ketene.^{5,6} This ring contraction corresponds to a Wolff rearrangement;⁷ it is also observed in the photolysis of α -diazoketones.⁸

Photohydrolysis (pathway b) is a minor pathway observed in acidic medium ($\phi_b = 0.012 \pm 0.001$ and 0.009 ± 0.001 for 2-ClPhOH and 2-BrPhOH, respectively⁴).

The third process consisting in the formation of an α -keto-carbene, 2-oxo-cyclohexa-3,5-dienylidene (pathway c) was demonstrated recently.⁴ This species ($\lambda_{\max} = 370$ and 388 nm) was firmly assigned on the basis of its characteristic triplet carbene reactions, that is addition onto molecular oxygen to yield the *ortho*-benzoquinone-*O*-oxide ($\lambda_{\max} = 475$ nm) and abstraction of an H atom from H-donors to give the phenoxyl radical ($\lambda_{\max} = 400$ nm). Addition of the α -ketocarbene on the starting molecule yields substituted biphenyls and abstraction of an H atom from H-donors like alcohols leads to phenol. This reactive behaviour is fully analogous to that of the related triplet carbenes, 4-oxocyclohexa-2,5-dienylidene⁹ and 4-imino-cyclohexa-2,5-dienylidene,¹⁰ produced in the heterolytic photodehalogenation of 4-halogenophenols and 4-halogeno-anilines, respectively. The absorption spectra of the three carbenes, featuring a characteristic two-peak structure, are also similar.^{4,9,10} Photochemical production of the α -ketocarbene was shown to be about ten times more efficient from 2-BrPhOH ($\phi_c = 0.04 \pm 0.01$) than from 2-ClPhOH ($\phi_c = 0.003 \pm 0.001$).⁴ This strong substituent effect is consistent with a mechanism in which intersystem crossing at the molecular level precedes carbene formation, since the intersystem crossing rate is expected to be higher in the molecule containing the heavier halogen atom.

In order to gain further insight into the primary steps of the reaction, we undertook a photochemical study of 2-iodophenol (2-IPhOH), which should exhibit even faster intersystem crossing through the heavy atom effect. On the other hand, the weakness of the carbon-iodine bond (64 kcal mol^{-1} ^{11–13}) could favour a homolytic cleavage process, which is not observed in the other 2-halogenophenols. Previous results obtained on related systems are conflicting: if no homolytic C–I scission was reported in the photolysis of aqueous 4-IPhOH,¹⁴ in contrast, the photolysis of 3-iodotyrosine in water was shown to produce 3-tyrosyl free radicals and iodine atoms.¹⁵ In this work, we report the photolysis of 2-IPhOH investigated by means of laser flash photolysis and product studies. Both the anionic and the molecular forms of the molecule ($pK_a = 8.46$ ¹⁶) were studied.

Experimental

Material and methods

2-IPhOH was purchased from Aldrich and purified by sublimation at room temperature before use. Phenol, pyrocatechol, 2-ClPhOH and 2-propanol were of the highest purity grade available and were used as received. Water was purified with a Milli-Q (Millipore) device. ¹H NMR spectra were recorded on a Bruker AC400 spectrometer. Mass spectrometry analyses were performed by the Service d'Analyse of the Université d'Orléans, France. UV-visible spectra were recorded on a Cary 3 (Varian) spectrophotometer. Analytical HPLC was carried out using a Waters apparatus equipped with a photodiode array detector and a conventional reverse phase 5 μm column. Pyrocatechol was titrated on a Merck apparatus equipped with a Hitachi F-1050 fluorescence detector; the mobile phase was a mixture of water with H_3PO_4 (0.1%) and MeOH (40–60, v/v). Preparative HPLC was performed on a Gilson apparatus with UV detection using a semi-preparative 3 μm Microsorb column.

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 or Quanta-Ray GCR-130-1, 266 nm, pulse duration 9 ns). The procedures used for transient absorption spectroscopy measurements have been described previously.^{17,18} Absorbances within the wavelength range 250–320 nm were corrected for bleaching.

Steady-state irradiations

Aqueous 2-IPhOH ($4 \times 10^{-4} \text{ mol l}^{-1}$) was irradiated at 282 nm using a high pressure xenon lamp (1600 W) and a Schoeffel monochromator. Potassium ferrioxalate was used as a chemical actinometer. Solutions were deoxygenated by argon bubbling for 20 min. prior to irradiation and were suroxygenated by oxygen bubbling. The pH was adjusted using HClO_4 or NaOH.

Identification of photoproducts

Phenol, pyrocatechol and cyclopentadienic acids were identified by reference to authentic samples. Cyclopentadienic acids dimerise in concentrated solutions¹ and do not exist as pure dry products. We prepared a solution of authentic cyclopentadienic acids by irradiating 2-ClPhO[−] (pH = 12) at 280 nm. Assuming a yield of photocontraction from 2-ClPhO[−] equal to 0.3,³ we could use this solution to quantify the formation of cyclopentadienic acids from 2-IPhOH. In preliminary experiments, we found that irradiating NaI in the presence of 2-IPhOH efficiently yielded the same biphenyls as the irradiation of 2-IPhOH alone. So, we chose to accumulate biphenyls using the following procedure: a 100 ml deoxygenated solution containing NaI ($6.8 \times 10^{-2} \text{ mol l}^{-1}$) and 2-IPhOH ($5.8 \times 10^{-3} \text{ mol l}^{-1}$) was irradiated at 254 nm in a quartz reactor using a germicide lamp. Three biphenyls were separated by preparative HPLC and analyzed by ¹H-NMR and mass spectrometry.

2-Iodo-6-(2'-hydroxyphenyl)phenol. λ_{\max}/nm (H_2O) 250 and 285; ¹H NMR (CD_3OD , 400 MHz): δ 8.28 (1H, d, *J* 2.0), 8.01 (1H, d, *J* 2.1), 7.91 (1H, dd, *J* 8.7 and 2.1), 7.71 (1H, d, *J* 2.5), 7.19 (1H, d, *J* 8.7); MS (EI): *m/z* 312, and fragments at 185 (40%), 157 (45), 128 (80).

2-Iodo-4-(2'-hydroxyphenyl)phenol. λ_{\max}/nm (H_2O) 252 and 295; ¹H NMR (CD_3OD , 400 MHz): δ 8.22 (1H, d, *J* 2.3), 7.86 (1H, dd, *J* 8.7 and 2.3), 7.41 (1H, d, *J* 2.5), 7.31 (1H, dd, *J* 8.7 and 2.2), 7.05 (1H, d, *J* 8.7); MS (EI): *m/z* 312, and fragments at 185 (50%), 157 (45), 128 (60).

4-(2'-Hydroxyphenyl)phenol or isomers. λ_{\max}/nm (H_2O) 247 and 285; MS (EI): *m/z* 186, and fragments at 167 (20%), 157 (40), 128 (35).

Results and discussion

Photolysis of 2-IPhOH

Laser flash photolysis experiments. Fig. 1 shows the transient spectra measured in a deoxygenated solution of 2-IPhO[−] ($2.0 \times 10^{-4} \text{ mol l}^{-1}$) at pH 12. Based on analogy to previous work,^{5,6} the pulse end transient exhibiting an absorption maximum around 255 nm was assigned to the ketene and the secondary species with maximum at 283 nm to the dianionic fulvene-6,6-diol, the former being converted into the latter with $k = 1.3 \times 10^6 \text{ s}^{-1}$. A further species absorbing in the near UV and decaying by a first-order kinetics with $k = 5.0 \times 10^5 \text{ s}^{-1}$ was detected at pulse end. Its two-band structure ($\lambda_{\max} = 388$ and 375 nm) was made clear by subtracting the

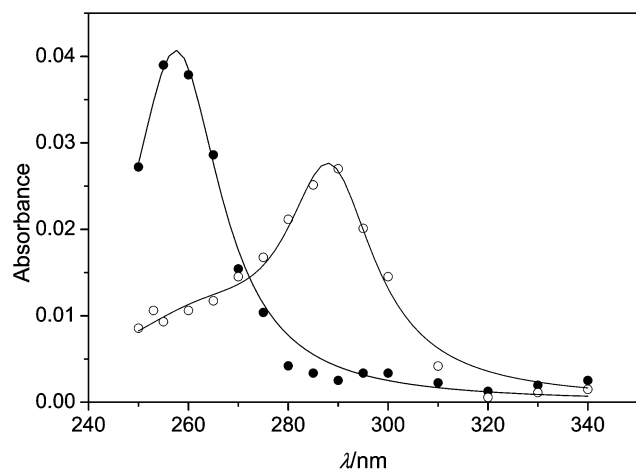


Fig. 1 Transient absorption spectra from aqueous 2-IPhO[−] at pH 12. Absorbances normalised to 2 mJ per pulse and corrected for bleaching, $A(266) = 0.28$. (●) extrapolated to pulse end, (○) measured 4 μ s after the pulse end.

absorbances measured 8 μ s after pulse end from those measured at pulse end (Fig. 2). This transient is similar to that produced upon irradiation of 2-BrPhOH and is therefore assigned to the α -ketocarbene.⁴ To firmly confirm this attribution, we photolysed 2-IPhO[−] first in the presence of oxygen (1.3×10^{-3} mol l^{−1}) and then in that of 2-propanol (0.17 mol l^{−1}). As expected, the 388 nm transient decay rate was significantly enhanced in both cases and secondary species were produced exhibiting spectral characteristics corresponding to those of *ortho*-benzoquinone-*O*-oxide⁴ and the phenoxyl radical,¹⁹ respectively (Fig. 3). The transient spectroscopy of 2-IPhO[−] is thus very similar to that of 2-BrPhOH.⁴

The irradiation of neutral 2-IPhOH also produced ketene and fulvene-6,6-diol, but in very low yields. In addition, a further transient showing a broad absorption band extending from 300 up to 500 nm with a maximum at 385 nm was detected (Fig. 4), reminiscent of the well-known I₂^{•−} radical anion.^{20–22} In order to confirm this assignment, we photolysed 2-IPhOH (5.0×10^{-4} mol l^{−1}) in the presence of NaI (6.2×10^{-4} mol l^{−1}) after ensuring that direct photolysis of NaI alone at this concentration did not produce I₂^{•−} radical anions in measurable amounts. As expected, the addition of NaI significantly enhanced the rate of formation of the 385 nm transient as well as the absorbance at 385 nm (Fig. 4 and insert). The observed formation rate constant

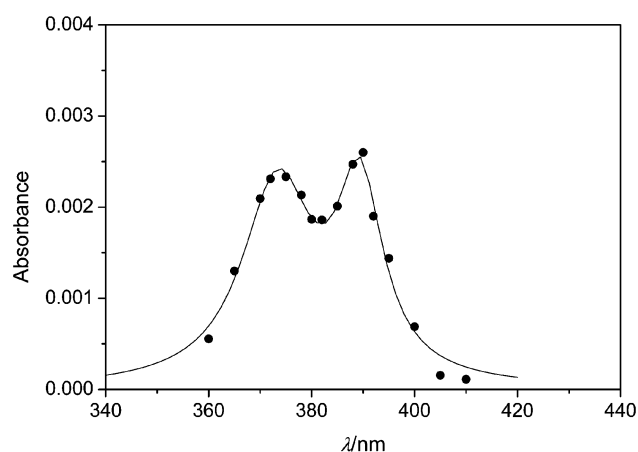


Fig. 2 Transient absorption spectra from deoxygenated aqueous 2-IPhO[−] at pH 12. Absorbances normalised to 2 mJ per pulse, $A(266) = 0.77$. Difference between the absorbances measured at pulse end and those measured 8 μ s after pulse end.

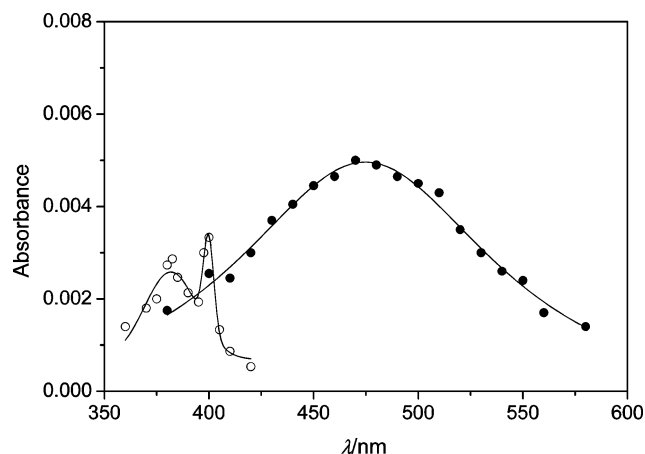


Fig. 3 Transient absorption spectra from aqueous 2-IPhO[−] at pH 12. Absorbances normalised to 2 mJ per pulse, $A(266) = 0.77$. (●) in oxygenated medium, (○) in deoxygenated medium containing 2-propanol (0.17 mol l^{−1}).

($k = 7.5 \times 10^6$ s^{−1}) was in excellent agreement with the known rate constant of reaction between I[•] and I[−] ($k = 1.1 \times 10^{10}$ mol^{−1} l s^{−1})^{20–22}. This result proves that C–I homolysis occurs from the molecular form of 2-IPhOH. The anionic form was also irradiated in the presence of NaI; the absorption of the I₂^{•−} radical was not detected in this case. Whether heterolytic α -ketocarbene formation also occurs from neutral 2-IPhOH was difficult to decide due to the overlapping absorption spectra of the carbene and of the I₂^{•−} radical. A careful examination of the end-of-pulse absorbances at 388 nm revealed, however, that α -ketocarbene formation was at least five times less in neutral than in basic medium.

All transients shown in Figs. 1–4 were formed in monophotonic processes as indicated by the linear dependences of their absorbances on the laser pulse energy, P (Fig. 5). Using chemical actinometry as described in ref. 18, we computed the product $\epsilon \times \phi$ of the quantum yield and extinction coefficient of each transient from the slopes of the regression lines. In basic medium, we found 2400 ± 400 mol^{−1} l cm^{−1} at 260 nm corresponding mainly to the ketene, 1750 ± 300 mol^{−1} l cm^{−1} for the dianionic fulvene-6,6-diol at 283 nm and 62 ± 15 mol^{−1} l cm^{−1} for the α -ketocarbene at 388 nm. In acidic medium, we obtained 120 ± 25 mol^{−1} l cm^{−1} for the fulvene-6,6-diol at 295 nm and 780 ± 120 mol^{−1} l cm^{−1} for the I₂^{•−} radical at 385 nm. Using $\epsilon = 2100$ mol^{−1} l cm^{−1} for the α -ketocarbene

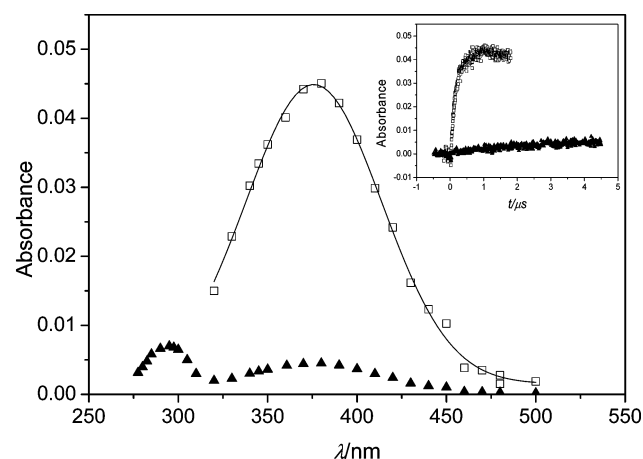


Fig. 4 Transient absorption spectra from aqueous neutral 2-IPhOH. Absorbances normalised to 2.2 mJ per pulse, $A(266) = 1.1$. (▲) measured 1 μ s after the pulse end in solution containing only 2-IPhOH, (□) measured 4 μ s after the pulse end upon addition of NaI (6.2×10^{-4} mol l^{−1}). Insert: time course of absorbances at 385 nm

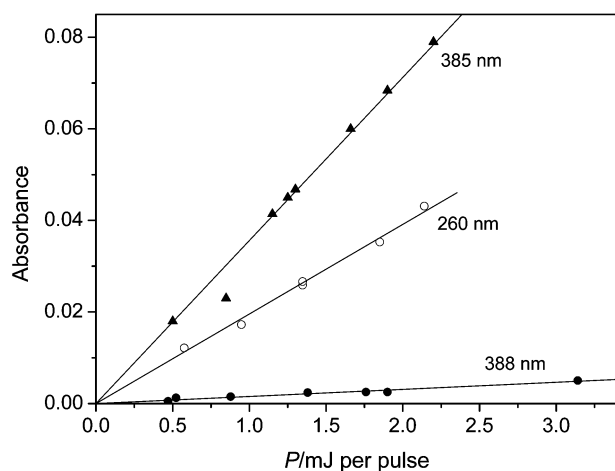


Fig. 5 Dependence of absorbance on laser pulse energy (P). (○) ketene at 260 nm in aqueous 2-IPhO[−], $A(266) = 0.41$; (●) α -ketocarbene at 388 nm in aqueous 2-IPhO[−], $A(266) = 0.77$; (▲) $I_2^{\bullet-}$ radical at 385 nm in aqueous 2-IPhOH containing NaI (6.2×10^{-4} mol l^{−1}), $A(266) = 1.1$.

at 388 nm,⁴ we compute $\phi_c = 0.03 \pm 0.01$ in basic medium and using $\varepsilon = 10\,000$ mol^{−1} l cm^{−1} for $I_2^{\bullet-}$ at 385 nm,²³ we get $\phi_r = 0.08 \pm 0.01$ in neutral solution. The $\varepsilon \times \phi$ value measured at 260 nm in basic medium cannot be used to evaluate the quantum yield of photocontraction accurately because the α -ketocarbene also contributes to absorption in the far-UV wavelength range.⁹

Steady-state irradiations. The quantum yield of 2-IPhOH photodegradation was measured in various conditions of pH and deoxygenation (Table 1). The formation of the main photoproducts (cyclopentadienic acids, pyrocatechol, phenol and biphenyls) was also studied. In basic medium, the quantum yield of 2-IPhOH photolysis is equal to 0.17 and cyclopentadienic acids are the only products observed; they account for about 70% of converted 2-IPhO[−]. In neutral or acidic solution, the quantum yield of 2-IPhOH photolysis is three times smaller than in basic medium and cyclopentadienic acids are produced in low yield in agreement with the results obtained by laser flash photolysis. In deoxygenated solution, biphenyls (mainly 2-iodo-4-(2'-hydroxyphenyl)phenol) are produced along with phenol; pyrocatechol is detected in traces. In oxygen-saturated medium, the mass balance is very poor. The formations of biphenyls and phenol are drastically reduced while the production of pyrocatechol is enhanced. In deoxygenated solution containing 2-propanol, the formation of biphenyls is reduced too and that of phenol is favoured.

Interpretation. The reaction pathways of 2-iodophenol photolysis emerging from the results presented above are summarised in Scheme 2.

Ring contraction and α -ketocarbene formation are the two dominant photoreaction pathways of 2-IPhO[−], with efficiencies around 0.11 and 0.03, respectively. All observable

photoproducts are due to photocontraction. The lack of detectable photoproducts originating from the carbene pathway in basic medium has already been noted in the case of the 4-halogenophenolates.^{9,24} The biphenyls expected from addition of the carbene on the substrate were found to be stable in highly basic medium and should be detected if formed. It must therefore be assumed that the intermediary cyclohexadiene-type moieties resulting from the addition reaction do not yield biphenyls under these pH conditions.

In acidic or neutral medium, ring contraction and α -ketocarbene formation are minor pathways, with efficiencies lower than 0.005, and photohydrolysis is also negligible. The main reaction route in this case is the formation of I^{\bullet} atoms through homolytic cleavage of the carbon-iodine bond ($\phi_r = 0.08$). The concomitantly generated hydroxyphenyl radicals (HOPh[•]) could not be detected by laser flash photolysis. Nevertheless, their formation is evidenced by the detection of 2-iodo-6-(2'-hydroxyphenyl)phenol and 2-iodo-4-(2'-hydroxyphenyl)phenol among the photoproducts, which result from the addition of HOPh[•] on the nucleophilic C² and C⁴ carbons of 2-IPhOH. This addition is inhibited both by 2-propanol and oxygen in accordance with the easy scavenging of HOPh[•].²⁵ In the first case, phenol is formed by reduction of HOPh[•], while, in the second one, pyrocatechol is the end product of HOPh[•] oxidation. In the chloro and bromo analogues, formation of pyrocatechol was observed whatever the oxygen concentration and it was proposed to result from hydrolysis *via* a heterolytic pathway. In the case of 2-iodophenol, pyrocatechol was observed in oxygenated medium only. Its mechanism of formation is therefore different; one possibility would be addition of oxygen onto a HOPh[•] radical, followed by a reduction step. The mass balance in neutral oxygenated medium being poor, pyrocatechol is only one of the possible end products of HOPh[•] oxidation.

A comparison of the photoreactivities of the 2-halogenophenols

A comparison of the respective efficiencies of the three photo-induced dehalogenation pathways in the 2-halogenophenol series (2-ClPhOH, 2-BrPhOH and 2-IPhOH) may serve to clarify the mechanism of their photoreactions (Table 2). The general mechanism deduced from this comparison is summarised in Scheme 3 (written for the anionic halogenophenols, but valid for neutral 2-ClPhOH and 2-BrPhOH as well).

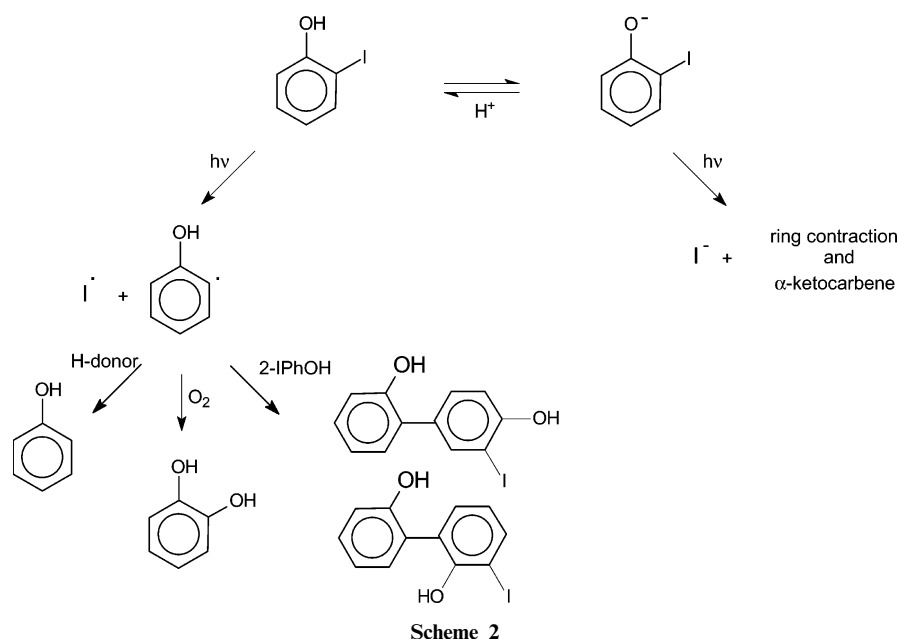
The cleavage of the C–X bond is always heterolytic except with 2-IPhOH for which the homolytic pathway is dominant ($\approx 90\%$). This specific behaviour, characteristic of the molecular form, can be explained by the low C–I bond energy (64 kcal mol^{−1} compared to 79–80 kcal mol^{−1} for C–Br^{11–13}).

The processes occurring after heterolysis are ring contraction, photohydrolysis and α -ketocarbene formation (Scheme 1). As can be seen in Table 2, changing the halogen atom has a significant effect on the efficiency of these processes. First, the photocontraction efficiency decreases in the order Cl > Br > I, the difference being small between Cl and Br but significant between Br and I. Second, it appears that α -ketocarbene formation is more efficient from the iodo and bromo derivatives than for the chloro derivative. The ratio

Table 1 Quantum yields of 2-iodophenol consumption (ϕ) and product formation

Conditions	ϕ	$\phi_{\text{cyclopentadienic acids}}$	$\phi_{\text{pyrocatechol}}^a$	ϕ_{phenol}^a	Detection of biphenyls
1.5 Argon	0.051 ± 0.006	0.003 ± 0.001	$< 10^{-5}$	0.010	Yes
Neutral Argon	0.065 ± 0.007	0.004 ± 0.001	$< 10^{-5}$	0.0070	Yes
Neutral Oxygen-saturated	0.047 ± 0.006	0.003 ± 0.001	0.0070	$< 10^{-4}$	No
Neutral Argon, 2-PrOH (0.17 mol L ^{−1})	0.061 ± 0.006	0.004 ± 0.001	$< 10^{-5}$	0.038	No
12.5 Argon	0.17 ± 0.02	0.11 ± 0.02	$< 10^{-5}$	$< 10^{-4}$	No

^a Estimated error $\pm 15\%$

**Table 2** Reaction pathways of 2-ClPhOH, 2-BrPhOH and 2-IPhOH

X	Form	Reference	Heterolytic cleavage			Homolytic cleavage ϕ_{X^\cdot}
			Photocontraction ϕ_a	Photohydrolysis ϕ_b	α -Ketocarbene formation ϕ_c	
Cl	Neutral	4	0.042 ± 0.008	0.012 ± 0.001	0.003 ± 0.001	0
	Anionic	1	0.30 ± 0.03		nd	
Br	Neutral	4	0.035 ± 0.007	0.009 ± 0.001	0.04 ± 0.01	0
	Anionic	3	0.27 ± 0.03		0.03 ± 0.01	
I	Neutral	This work	0.004 ± 0.002	$< 10^{-5}$	< 0.005	0.08 ± 0.01
	Anionic	This work	0.11 ± 0.02		0.03 ± 0.01	

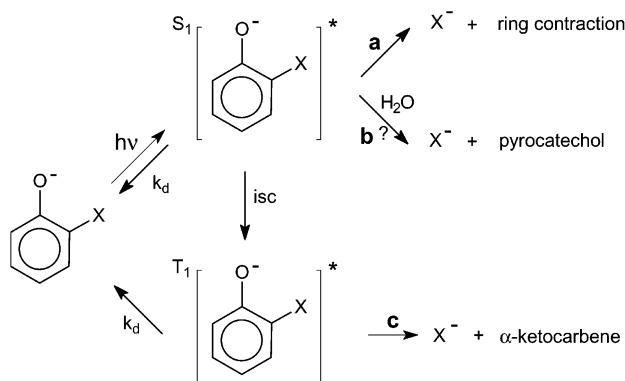
nd: not determined

of the carbene formation yield to the photocontraction yield for the anionic forms increases from bromo to iodo (0.11 against 0.27). Based on the action of the internal heavy atom effect, these two observations are consistent with pathway a arising from the singlet excited state and pathway c from the triplet excited state. The first conclusion is consistent with the general view of the photo-Wolff rearrangement as proceeding on the excited singlet surface.^{7,26} The second conclusion is in line with the characteristic triplet reactivity of the α -ketocarbene. The quantum yield of 2-IPhO⁻ photolysis is not as high as expected; this may be explained by fast non-radiative deactivation processes. Lastly, the efficiency of photodrolysis,

while very low, also decreases in the order Cl > Br > I, suggesting that this reaction may take place from the singlet excited state, too.

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