Photochemical transformation of aqueous *para*-halogenophenylureas: evidence for the intermediary formation of carbenes

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L e t t e r

N-Substituted 4-iminocyclohexa-2,5-dienylidenes ($\lambda_{max} = 300$ and 405 nm) are detected at pulse end upon laser flash photolysis of aqueous monuron and metobromuron. In oxygenated medium these carbenes are converted into N-substituted iminoquinone-O-oxides ($\lambda_{max} = 300$ nm and 460 nm) and in the presence of H-donor molecules into N-substituted anilino radicals ($\lambda_{max} = 430$ nm).

Substituted phenylureas exhibit herbicidal activity and are widely used as plant products. After application they are subject to photolysis and it is therefore of great interest to determine their mechanisms of phototransformation.[1] The photochemical transformations of *para*-chlorophenyl-*N,N*-dimethylurea (monuron) and *para*-chloro- or *para*-bromophenyl-*N,N*-methoxymethylureas (monolinuron and metobromuron) were investigated in the past.[2–6] Many photoproducts were found, depending on the experimental conditions. Dehalogenation with hydroxylation was observed at low substrate concentration (2×10^{-5} M),[2] whereas formation of numerous biphenyls was reported at higher concentration (10^{-3} M).[3,4] Demethylation or demethoxylation of the substituted ureas were observed in all cases. Reductive dechlorination was shown to occur in place of photohydrolysis in water containing surfactants or in methanol.[5,6]

These analytical results resemble those obtained by photolysis of *para*-halogenophenols and *para*-halogenoanilines in water[7–12] and explained by the formation of carbenes as primary intermediates[10–12] (Scheme 1). These species, produced after heterolytic loss of HX or X$^-$, were successfully detected by nanosecond laser flash photolysis in aqueous medium and at ambient temperature.[10–12]
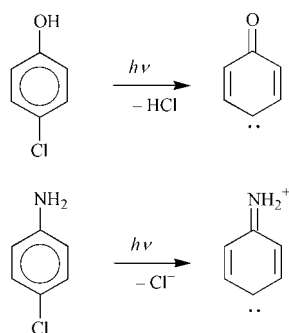
Scheme 1

The carbene 4-oxocyclohexa-2,5-dienylidene, which was generated for the first time at cryogenic temperatures by photolysis of the corresponding quinone diazide and characterized by matrix isolation spectroscopy,[13–15] has an absorption spectrum showing a two-band structure with maximum at 370 and 384 nm. The carbene 4-iminocyclohexa-2,5-dienylidene, produced by photolysis of aqueous *para*-halogenoanilines, absorbs at 390 and 407 nm.[12] Both carbenes exhibit the characteristic reactivity of triplet carbenes, adding oxygen to give the benzoquinone oxide[16,17] or the iminoquinone-O-oxide[12] and abstracting an H atom from aliphatic alcohols to yield the phenoxyl radical[17] or the anilino radical cation.[12] The addition of the carbene onto a starting molecule yields dimers and the reaction with H_2O gives rise to hydroquinone or aminophenol.

To determine the mechanism of phototransformation of monuron (M) and metobromuron (MB) in water and detect eventual carbenes, we investigated the reactions by means of laser flash photolysis and transient absorption spectroscopy.

The photolysis of deoxygenated and neutral aqueous solutions of MB (2×10^{-4} M) produces the transient absorption spectra shown in Fig. 1. The spectrum observed at pulse end exhibits two bands with maxima at 300 and 405 nm. Another species grows in during the first microseconds following the pulse end (Fig. 1, insert). It absorbs at longer wavelength ($\lambda_{max} = 440$ nm) and is long-lived. In air-saturated medium, the 300/405 nm transient is detected again at pulse end. A different species, absorbing strongly with maxima at 300 and 460 nm (Fig. 2), appears in the 4 µs following the pulse end (Fig. 2, curve A of insert). The growing in is made faster by an increase of the oxygen concentration: the apparent first-order rate constant of formation is equal to 6.6×10^5 s^{-1} in air-saturated medium and to 2.9×10^6 s^{-1} in oxygen-saturated solution. This species decays slowly ($k_d = 1.0 \times 10^4$ s^{-1}). Lastly, in nitrogen-saturated solution containing 2-propanol (0.17 M), a species with an absorption maximum at 430 nm is
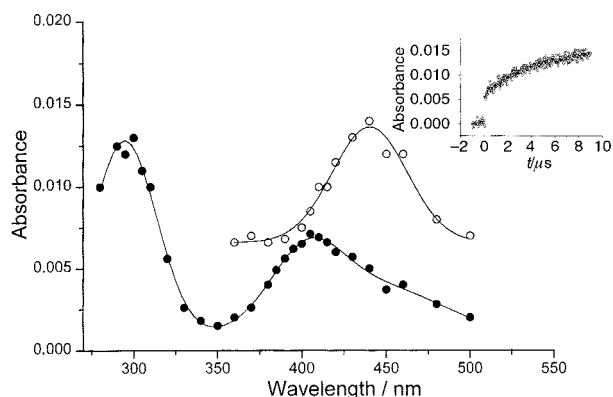
Fig. 1 Transient spectra measured from a nitrogen-saturated aqueous solution of MB (2×10^{-4} M); $A(266) = 0.60$; $P = 1.6$ mJ pulse^{-1}: (●) at pulse end, (○) 8 µs after pulse end. The insert shows the absorbance time course at 440 nm.
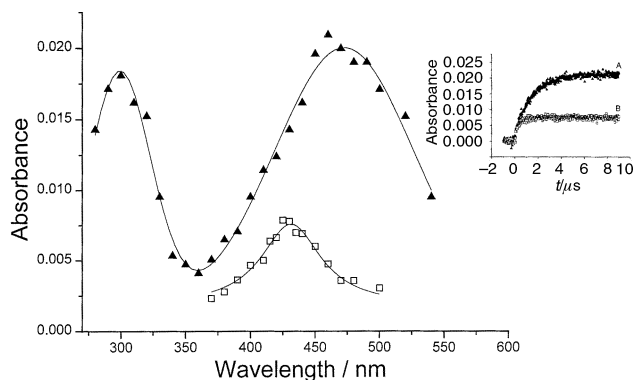
Fig. 2 Transient spectra measured from an aqueous solution of MB (2×10^{-4} M); $A(266) = 0.60$; $P = 1.6$ mJ pulse^{-1}: (▲) 6 μs after pulse end in an air-saturated solution, (□) 2 μs after pulse end in an N$_2$-saturated solution containing 2-propanol (0.17 M). The insert shows the absorbances time courses (*A*) at 450 nm in an air-saturated solution and (*B*) at 430 nm in an N$_2$-saturated solution containing 2-propanol (0.17 M).

Fig. 3 Dependence on pulse energy of the absorbances of species obtained from photolysis of MB (2×10^{-4} M): (●) at pulse end at 410 nm in an N$_2$-saturated solution; (▲) 6 μs after pulse end at 450 nm in an air-saturated solution; (□) 2 μs after pulse end at 430 nm in an N$_2$-saturated solution containing 2-propanol (0.17 M).

detected (Fig. 2). It reaches a maximum concentration 2 μs after the pulse end (Fig. 2, curve B of insert). The apparent first-order rate constant of formation is equal to 3.0×10^6 s^{-1}.

The photolysis of M in water yields transient species exhibiting the same absorption spectra and the same reactivity as those obtained from MB. It proves that dehalogenation has occurred, considering that the presence of Cl or Br on the aromatic ring should induce a shift of several nm in the absorption maxima of the transient species observed. To detect the eventual formation of chloride radicals, we photolyzed M in the presence of Cl$^-$ (10^{-2} M). No absorption due to the Cl$_2^{\cdot-}$ radical anion was observed within the wavelength range 330–360 nm,[19] showing that dehalogenation is not homolytic.

All the transients are formed by monophotonic processes as indicated by the linear dependences of the absorbances with *P*, the laser pulse energy (Fig. 3). Based on actinometry with K$_2$S$_2$O$_8$, the $\varepsilon \times \phi$ values were evaluated. Data are listed in Table 1.

The transients observed upon photolysis of M and MB show strong analogies with those obtained by photolysis of *para*-chlorophenol and *para*-chloroaniline[10–12] and the 300/405 nm transient is likely to be a carbene and the precursor of all the other species observed. Unfortunately, the overlapping of the absorption spectra prevented us from verifying that in each case the rate of disappearance of the 300/405 nm transient corresponds to the rate of formation of the secondary transient. The 440 nm transient formed in deoxygenated solutions may be an intermediate produced by addition of the carbene onto a starting molecule or water and yielding biphenyls in the former case and a hydroxylated product in the latter. The 300/460 nm transient observed in oxygenated
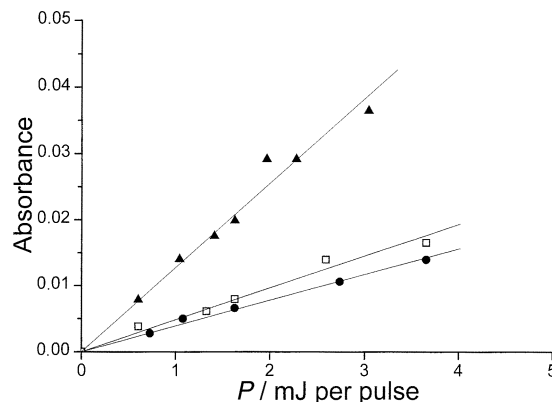
medium exhibits the same spectral characteristics (broad unstructured band) and the same kinetics of formation ($k = 2.3 \pm 0.2 \times 10^9$ M^{-1} s^{-1}) as the iminoquinone-*O*-oxide[12] produced by addition of oxygen onto the carbene and should be the *N*-substituted iminoquinone-*O*-oxide. Lastly, the 430 nm species formed in solutions containing 2-propanol should be the *N*-substituted anilino radical. To prove this assignment, we produced this radical independently by photolyzing solutions containing 1,1-dimethyl-3-phenylurea and K$_2$S$_2$O$_8$. In this way, sulfate radicals are photogenerated; they oxidize the phenylurea in a one-electron process[20] and the *N*-substituted anilino radical is expected to be produced by further deprotonation of the radical cation. The absorption spectrum measured from this reaction mixture 30 μs after pulse end (Fig. 4) is similar to that observed in solutions containing MB and 2-propanol. It confirms that the 430 nm species is the *N*-substituted anilino radical.

The carbene 4-iminocyclohexa-2,5-dienylidene was shown to absorb at shorter wavelengths (*ca.* 15 nm) than the anilino radical cation, both species exhibit a two-band absorption spectrum.[12] The carbenes derived from M and MB also have an absorption band blue-shifted by 25 nm compared to the *N*-substituted anilino radical, but contrary to their unsubstituted counterparts, they show an unstructured absorption band.

To determine the quantum yields of carbene formation we photolyzed M and MB at 266 nm using low intensity continuous light. 2-Propanol (0.17 M) was added to effect the reduction of the carbenes. The quantum yields of substrate loss are found to be equal to 0.068 ± 0.008 and 0.12 ± 0.01, respectively, whereas those of reduction photoproduct formation (1,1-dimethyl-3-phenylurea in the case of M) are equal to 0.051 ± 0.008 and 0.060 ± 0.008. Assuming a complete reduction of carbenes, we deduce that the quantum yields of

Table 1 Values of $\varepsilon \times \phi$ products and estimated ε

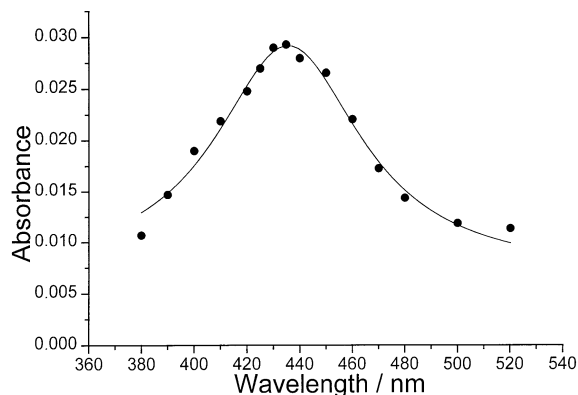| Transient (λ_{max}/nm)	$\varepsilon \times \phi$/M^{-1} cm^{-1}		ε/M^{-1} cm^{-1}
	MB	M	
N-substituted 4-iminocyclohexa-2,5-dienylidenes (300/405)	220 ± 40 at 410 nm	210 ± 40 at 410 nm	3800 ± 800 at 410 nm
N-substituted iminoquinone-*O*-oxides (300/460)	670 ± 100 at 450 nm	680 ± 100 at 450 nm	$11\,000 \pm 2000$ at 450 nm
N-substituted anilino radicals (430)	260 ± 40 at 430 nm	220 ± 40 at 430 nm	4300 ± 800 at 430 nm

Fig. 4 Spectrum of the *N*-substituted anilino radical measured 30 μs after pulse end in a solution containing 1,1-dimethyl-3-phenylurea $(5 \times 10^{-4}$ M) and $K_2S_2O_8$ (0.1 M) at pH 3.

carbene formation are equal to 0.051 and 0.060, respectively. On the basis of these data, the ε values were estimated (see Table 1). These data show that the carbene pathway is not the only route of reaction of MB and M. As previously reported,[2–6] demethylation or demethoxylation occur too.
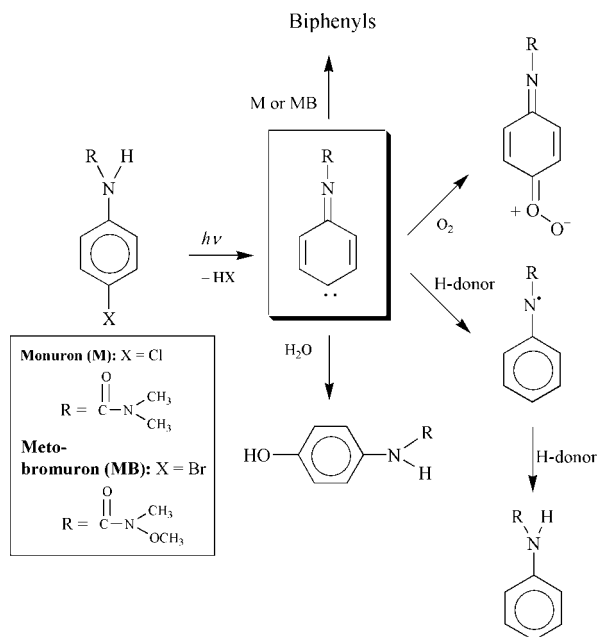
Scheme 2

In conclusion, carbenes are produced upon irradiation of monuron and metobromuron in water. The reaction mechanism *via* the carbene pathway is given in Scheme 2.

Experimental

M and MB were purchased from Aldrich (St Quentin-Fallavier and used as received. The water was purified using a Milli-Q device (Millipore). The laser flash photolysis was performed using a frequency-quadrupled Nd : YAG laser (Quanta Ray GCR130, pulse duration 9 ns, $\lambda_{exc} = 266$ nm[18]). Steady state irradiations were performed using a high pressure xenon lamp equipped with a Schoeffel monochromator. Substrate consumption was measured by HPLC (UV detection, conventional reversed phase column).

Notes and references

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