

## Flash Photolysis-HPLC Method applied to the Study of Photodegradation Reactions

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A new method, involving UV flash photolysis followed shortly by HPLC analysis of products, has been applied to the study of the partial photooxidation of 4-chlorophenol as an example of an oxidative photodegradation reaction of pollutants.

The conventional methods for the study of photochemical reactions in solution usually involve irradiation of the solution with a steady-state light source for an extended period of time, followed by analysis using an appropriate analytical method. One of the difficulties with these methods is that, for reactions which may involve many photochemical steps, photolysis of intermediate products makes the analysis of reaction steps difficult. If initial concentrations are increased so as to be able to study the reaction at a lower conversion fraction, the possibility of bimolecular reaction steps may change the mechanism and lead to different products.

We have initiated a study of the photodegradation reactions of organic pollutants in aqueous solution.<sup>1</sup> These pollutants are usually found in natural water systems at very low concentrations, and so we had to develop a new approach to study the reaction sequences under environmentally meaningful conditions. We have utilized the technique of flash photolysis; however, instead of using the conventional configuration where subsequent reactions are followed by detect-

ing the optical absorption of transients, we have employed HPLC detection to identify moderately-lived (>15 min) intermediates. With this approach we can obtain a significant conversion fraction with a single flash, and thus avoid the possibility of photolysis of intermediates. Also by using multiple flashes, we can follow the sequence of intermediates in the reaction.

4-Chlorophenol **1** was chosen as a model compound for testing our new method, as the photooxidation of this compound has been studied by Boule *et al.*<sup>2</sup> using conventional methods. These authors found that the reaction was nonspecific giving hydroxy-*p*-benzoquinone, along with polyphenolic oligomers and other products.

Aqueous solutions (*ca.* pH 5) of **1** ( $10^{-5}$ – $10^{-3}$  mol dm<sup>-3</sup>) were photolysed with 1–30 flashes (40–50 J), followed quickly by HPLC analysis. HPLC analysis of air equilibrated aqueous solutions ( $6.3 \times 10^{-4}$  mol dm<sup>-3</sup>) of **1** following a single flash indicated that *p*-benzoquinone **2** is the only primary product, since **2** is formed in almost stoichiometric amounts (>98%) from **1**. After 5–10 flashes, new products begin to appear: hydroxy-*p*-benzoquinone **3** and hydroquinone **4**. These are known products from the UV irradiation of **2** in aerated aqueous solutions.<sup>3</sup> After 20–30 flashes, traces of 1,2,4-trihydroxybenzene and 4-chlorocatechol can be observed.

Fig. 1 shows the depletion of **1** and the formation of the photoproducts as a function of the number of flashes. **2** rises sharply with a small number of flashes, but reaches a maximum as the photochemistry of **2** becomes important.

We postulate that the sequence of steps in the photodegradation of **1** is as in Scheme 1.

The amount of photodegradation of **1** does not change significantly with pH between pH 5 and 12. However, above *ca.* pH 12, the primary photoproduct changes from **2** to **3**. This is consistent with the known dark chemistry of **2** in alkaline solutions.

When bubbled with a gas stream containing progressively lower partial pressures of oxygen the yield of **2** dropped off significantly indicating that the photoreaction probably involves reaction of oxygen with the excited state of **1**.

When the concentration of **1** was increased above  $10^{-3}$  mol dm<sup>-3</sup>, **2** was still the major photoproduct, but evidence for many coupling products was obtained.

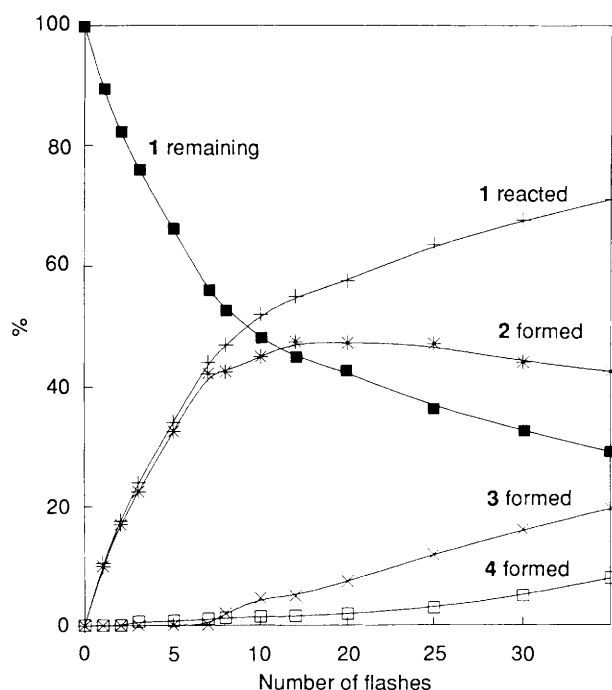
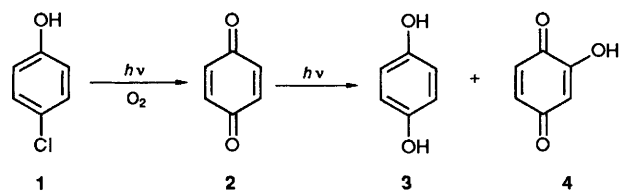


Fig. 1 Mole fractions (%) of reactant and products present in an aqueous solution (initially  $6.3 \times 10^{-4}$  mol dm<sup>-3</sup>) of 4-chlorophenol after being subjected to a number of flashes (45 J). Detection was by HPLC analysis.



Scheme 1

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After several flashes the pH was observed to decrease in unbuffered solution. This is expected as the removal of chlorine in the conversion from **1** to **2** should produce HCl.

In conclusion we have established that the photoreaction of **1** in oxygenated aqueous solutions proceeds very cleanly to produce **2** as the only photoproduct; **2** may then undergo further photoreaction. Our conclusions are at variance with the scheme suggested by Boule *et al*.<sup>2</sup> however, they studied this system at much higher concentrations of **1**.

The new method we have developed appears to be effective

for studying the sequence of photochemical reactions, particularly at low concentrations.

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#### References

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