Products and intermediates formed during the biacetyl-sensitised photo-oxidation of some azo dyes

J G Neevel, (the late) H C A van Beek and B van de Graaf*

Laboratory for Organic Chemistry and Catalysis, Delft University of Technology, PO Box 5045, 2600 GA Delft, The Netherlands

The flash irradiation for a few microseconds of aqueous aerobic solutions of biacetyl (2,3-butanedione) and a number of different *o*-arylazonaphthols resulted in the formation of the corresponding diazonium ions and α-naphthoquinones. This was verified from the intermediate spectra obtained after the flash. Verification for the formation of diazonium ions was also obtained from flow experiments, in which the diazonium ion was identified by coupling it to H-acid, forming a new azo compound. Less than equimolar formation of the diazonium ion from one of the azo dyes investigated indicated the occurrence of side reactions in which diazenyl radicals could play a role.

INTRODUCTION

The technique of flash photolysis can be used to elucidate the mechanisms of photochemical processes [1]. For example, it has been applied to study the intermediates formed during photofading of azo dyes in solution [2] and in a polymer matrix [3]. In a previous paper we described the biacetyl-sensitised photo-oxidation of some tautomeric azo dyes in aqueous solution as a model for the fading of azo dyes on non-protein substrates in the presence of oxygen [4]. This oxidative fading was very efficient, with quantum yields ranging up to 0.44. Fading was inhibited by phenol and other compounds that quench the intermediate triplet state of biacetyl [5]. Using flash photolysis, we determined reaction rate constants for the fading process [6]. The observed reaction rates excluded the possibility that singlet oxygen was the main oxidative species because of its short lifetime in aqueous systems. Therefore we proposed an oxidation mechanism with the diradical adduct formed by addition of oxygen to triplet biacetyl as the main oxidative species. We now report on further results from flash photolysis and continuous irradiation experiments carried out to analyse the reaction intermediates formed during oxidative fading of azo dyes.

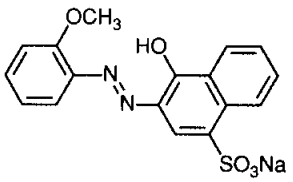
EXPERIMENTAL

Materials

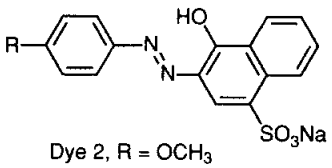
The origin and analysis of dyes 1–4 have been described elsewhere [4]. The disodium salt of H-acid (1-amino-8-naphthol-3,6-disulphonic acid, disodium salt; Fluka, 65–80%) was used as a naphthol coupling component in the flow analysis of the diazonium ion formed by photolysis of dye 4. For spectrophotometric identification, dye 5 was synthesised by naphthol coupling of diazotised *p*-bromoaniline to H-acid in alkaline solution. The dye was purified by recrystallisation (aqueous sodium chloride/ethanol) and dried in vacuum over phosphorus pentoxide. Thin layer chromatography on cellulose (2.5% ammonia) showed a minor impurity supposed to be the disazo dye. Structures of the investigated dyes are shown in Figure 1.

Methods

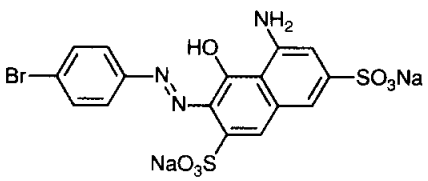
Flash photolysis experiments were carried out on the dyes 1 and 2 with the laboratory-built apparatus described previously [6]. The applied voltage of the flash was 8 kV (flash energy 0.64 kJ). Changes in transmission of the aerobic aqueous solution of the dyes (about 4–5 μmol/l) and biacetyl (0.025 mol/l) were measured after the flash as a function of time at different wavelengths. These were set



Dye 1, CI Acid Red 4



Dye 2, R = OCH_3
Dye 3, R = Cl
Dye 4, R = Br



Dye 5

Figure 1 Structures of azo dyes 1–5; the structures show the azo tautomers, but in solution these dyes exist largely as hydrazones [7,8]

* To whom correspondence should be addressed

at fixed wavelength intervals of 10 nm. The intervals were chosen between 310 and 460 nm for dye 1 and between 290 and 440 nm for dye 2, according to the spectra of the expected products (i.e. substituted diazonium ions and α-naphthoquinone-4-sulphonate). Changes in the absorbance (D) of the solutions were calculated from the measured transmissions by using the Lambert–Beer law. After correcting the results obtained to take account of dye fading, the net changes were plotted as a function of wavelength, thus obtaining the spectra of the products of dye fading.

Flow experiments were carried out by irradiating the aqueous solution of an azo dye (about 7 μmol/l) and biacetyl (0.05 mol/l) with u.v. lamps (two Philips TLADK 30/W05 fluorescent lamps) while it was pumped through a spiral quartz tube. The irradiated solution was circulated through a quartz cuvette placed in a u.v.–visible light spectrophotometer (Shimadzu UV-160), with which the spectra were obtained immediately after irradiation. Transient spectra were determined by subtracting the spectrum obtained before irradiation from that of the irradiated solution and correcting it with the dye spectrum for the amount of dye faded.

In a different approach the irradiated solution of dye 4 and biacetyl (0.1 mol/l) was mixed with a solution containing the naphthol coupling component H-acid (0.01 mol/l, as its disodium salt) and sodium hydroxide (0.01 mol/l). The formation of the new azo dye (dye 5), which had a maximum absorption at a higher wavelength than that of dye 4, was demonstrated by measuring the absorption spectrum of the solution and comparing the product spectrum with that of the synthesised dye 5.

For product analysis, aqueous solutions of dyes 1 or 2 (approx. 10^{-4} mol/l) and biacetyl (approx. 0.5 mol/l) were irradiated at 365 nm (Camag u.v. lamp) while air was bubbled through. The photolysed solutions were extracted with diethyl ether and the extracts were washed three times with water and dried with magnesium sulphate. After partial removal of the solvent, they were analysed by combined gas chromatography (column CP Sil 5 CB) and mass spectrometry (VG 70 SE).

RESULTS AND DISCUSSION

Irradiating an aerobic aqueous solution of dye 2 and biacetyl with a 20 μs flash resulted in the formation of certain products, the observed composite spectrum of which after 5 ms is shown in Figure 2 (white circles). This spectrum features a strong absorption maximum at about 308 nm, which coincides well with that of *p*-methoxybenzenediazonium fluoroborate (white squares) given in the literature (i.e. 313 nm [9–12]). The difference of 5 nm in the wavelength of the maximum was caused by superimposition of the spectrum of the α-naphthoquinone-4-sulphonate ion (black squares). The change in absorbance at 310 nm varied in direct proportion with the amount of dye faded, as shown in Figure 3. The slope of this line had a value of 15 700 l/(mol cm). Assuming that the α-naphthoquinone-4-sulphonate ion was formed in equimolar proportion from the dye, the measured extinction coefficient of sodium α-naphthoquinone-4-sulphonate at 310 nm (i.e. 2160 l/(mol cm)) was subtracted from this value. The resulting extinction coefficient (13 540 l/(mol cm)) was considerably lower than the values given in literature for the extinction coefficient of the *p*-methoxybenzenediazonium ion (25 000 [9,11] and 19 200 [10]). The ratio between the amount of diazonium formed and the extent of dye fading must therefore be lower than unity (about 0.54–0.70).

In a previous publication we presented a mechanism for the oxidative fading of *o*-arylazonaphthols in the presence of biacetyl [6]. The first step causing dye fading was assumed to be the formation of a dye radical through hydrogen abstraction from the dye by the diradical adduct formed by addition of oxygen to triplet biacetyl (Scheme 1). The second step was the nucleophilic addition of a perhydroxy radical (formed by dissociation of the hydrogenated diradical adduct arising from the first step) to the dye radical. In a third step the diazonium ion would be

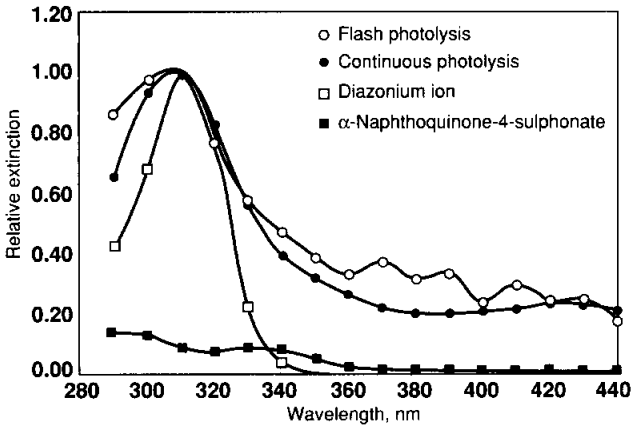


Figure 2 Product spectra of the oxidative fading of dye 2 in an aerobic aqueous solution of biacetyl; also shown relative to each other are spectra of *p*-methoxybenzenediazonium [9] and α-naphtoquinone-4-sulphonate

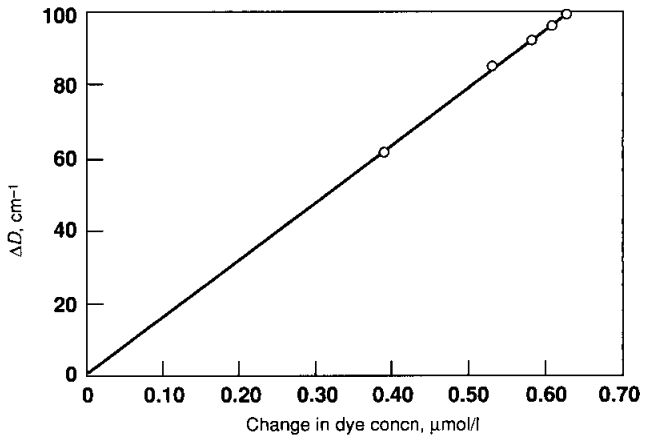
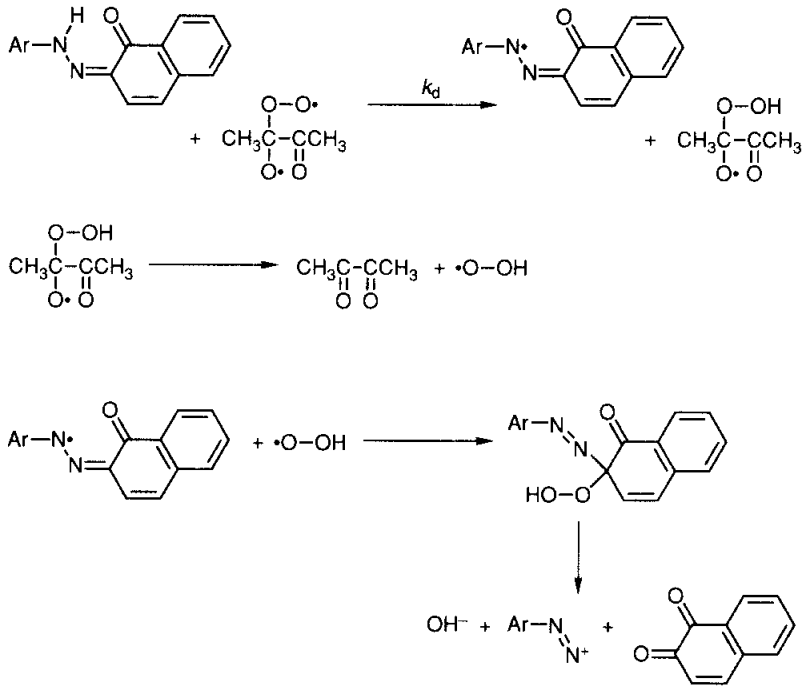


Figure 3 Change in absorbance at 310 nm as a function of the change in dye concentration during flash photolysis of an aqueous solution of dye 2 and biacetyl



Scheme 1

formed by dissociation of the adduct. The existence of a linear relationship between the amount of diazonium ion and the amount of dye faded (Figure 3) indicates that the second and third steps must be faster than the first ($k > k_d \approx 2 \times 10^8$ l/(mol cm) [6]). The ratio of 0.54–0.70 found for formation of the *p*-methoxybenzenediazonium ion from the dye indicates the simultaneous occurrence of different degradation routes for the dye.

A possible explanation could be that the diazonium ions are formed in some excited electronic state which either reacts further or is quenched to the ground state. The excited diazonium ions are believed to form charge-transfer complexes with suitable electron donors (i.e. the dye) [13–15]. Electron transfer then leads to the formation of diazenyl radicals that will decompose into molecular nitrogen and phenyl radicals [13–16]. By abstracting a hydrogen from the dye or biacetyl, the latter form anisole in the case of the dye 2. Anisole has indeed been detected by combined gas chromatography and mass spectrometry in the product mixture obtained by photolysis of concentrated solutions of dye 2. Electron transfer as well as hydrogen transfer are known to take place at very high rates (10^{10} l/(mol cm) [13]) and could well occur concurrently with the quenching of the excited diazonium ion, which also will be a fast process [14].

N.m.r. spectrometry has previously been used to identify α-naphthoquinone in the diethyl ether extracts of photolysed aqueous solutions of some azo dyes [4]. The equivalent product of the photolysis of dyes 1–4, α-naphthoquinone-4-sulphonate, could not be identified from the product spectrum (Figure 2). The product spectrum shows stronger absorptions in the region between 340 and 440 nm than can be explained solely by the measured spectrum of sodium α-naphthoquinone-4-sulphonate (white circles in Figure 2), shown proportional to the extinction of the diazonium ion. Therefore there are other products formed that absorb in this region.

The product spectrum derived by continuous irradiation in a flow experiment (black circles in Figure 2) shows the same maximum as that derived by the flash experiment. This indicates that the diazonium ion is quite stable and remains in the reaction mixture for several minutes.

With dye 1, the *o*-methoxy-substituted isomer of dye 2, the product spectrum obtained by flash photolysis featured a local maximum at 340 nm. According to literature [9], the *o*-methoxybenzenediazonium ion has its maximum absorbance at 356 nm, but its extinction coefficient (4900 l/(mol cm) [9]) is substantially lower than that of its *p*-substituted counterpart. If the spectrum of α-naphthoquinone-4-sulphonate is added to this, the resulting spectrum has a maximum at 340 nm, just as observed in the present work. As with dye 1, a linear relationship between the increase in absorbance at 360 nm and the amount of dye faded was observed; the slope of this line had a value of 6300 l/(mol cm). After subtracting the extinction coefficient for the quinone at 360 nm (i.e. 800 l/(mol cm)), the resulting extinction coefficient (5500 l/(mol cm)) was slightly higher than the literature value for the *o*-methoxybenzenediazonium ion given above. Contrary to the findings for dye 2, the side reaction described above will therefore play a minor role with dye 1. Anisole has been identified in the photolysate of dye 1 too, but this could also have been formed from photo-excited diazonium ions during the continuous irradiation applied here. In contrast to its *p*-isomer, the *o*-methoxybenzenediazonium ion absorbs at 365 nm.

The product spectra obtained after continuous irradiation of dyes 3 and 4 also showed maxima at or near the wavelengths expected for the diazonium ions (*p*-chloro $\lambda_{max} = 281$ nm; *p*-bromo $\lambda_{max} = 293$ nm [10]).

Formation of the diazonium ion was confirmed for dye 4 by showing that the photolysed solution formed a new azo dye (dye 5) after mixing it with an alkaline solution of H-acid (pH approx. 12). The product spectrum, corrected for the spectrum of dye 4 (Figure 4) was compared with that of the synthesised dye 5 in Figure 4; their similarity is evident.

CONCLUSIONS

Substituted *o*-phenylazonaphthols are rapidly oxidised to substituted α-naphthoquinones and substituted benzenediazonium ions following irradiation in aerobic aqueous solutions containing biacetyl. The benzenediazonium ions react with water to produce substituted phenols. The mechanism most likely proceeds via perhydroxy radicals. The diazonium ions are probably formed in an excited electronic state, and quenching to the ground state will concur with electron transfer from suitable electron donors to form diazenyl radicals which, in turn, will decompose into molecular nitrogen and phenyl radicals. The latter will abstract hydrogen to form substituted benzenes.

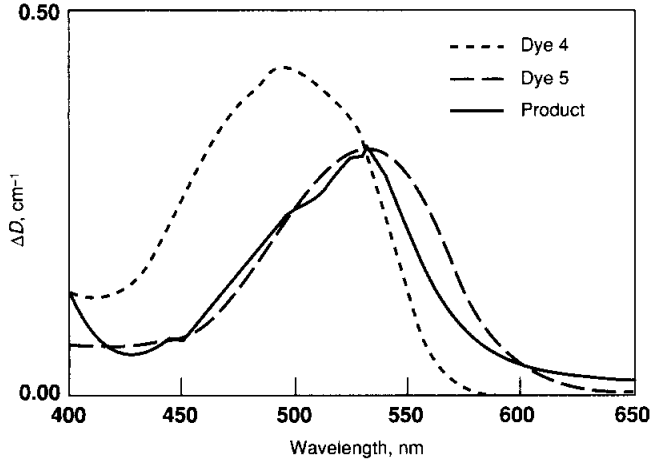


Figure 4 Corrected product spectrum after mixing of a photolysed aqueous solution of dye 4 with an aqueous alkaline solution of H-acid, and spectra of dyes 4 and 5

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