PERKIN 2

Free radical induced oxidation of the azo dye Acid Yellow 9

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The kinetics and mechanism of the free radical oxidation of the azo dye, Acid Yellow 9, by sulfate radical anions and hydroxyl radicals have been studied using pulse radiolysis and product analysis. Sulfate radicals react *via* one electron oxidation, generating the dye radical cation, which has an absorption maximum centered on 470 nm. In basic solutions, the radical cation mainly undergoes deprotonation to yield the aminyl radical which has a strong absorption with a maximum centered on 370 nm, and the pK_a for the radical cation is 5.5. Formation of a sulfated product, **1**, is indicative of a coupling reaction between the radical cation and sulfate radical anions. Studies also indicate that the hydroxyl radicals react with the dye by both electron transfer as well as by adduct formation.

Introduction

Azo dyes are a class of synthetic dyes, which find a variety of applications in the textile, paper, cosmetic, drug and food industries.[1] In many of these applications resistance of the dyes to free radical oxidation can lead to an improvement in the quality of the product. These dyes on colored fabrics can be severely impacted when laundered with commercial bleaches. Deleterious radical reactions with dyes are thought to be prompted by the adventitious presence of transition metals in the wash water or fabric itself with the peroxygen bleaches. Due to the extensive use of these dyes in the industry, discharge of these dyes through industrial effluents also represents a major environmental hazard. Several advanced oxidation processes including photochemical ones have been proposed for the removal of textile dyes from industrial effluents.[2–7] For such processes to be commercially viable, the susceptibility of these dyes to free radical induced oxidation is an essential requirement. A detailed understanding of the reaction mechanism involved in the free radical induced oxidation, would therefore make it possible to provide conditions under which the dyes could be made increasingly stable or susceptible to free radical induced oxidation. In view of this, we have undertaken a detailed study on the mechanism of free radical induced oxidation of commercially used azo dyes. Here we report on the elucidation of the mechanism of oxidation of the azo dye, Acid Yellow 9 by $SO_4^{\bullet -}$ and $OH^{\bullet}$ radicals, using the methodologies of pulse radiolysis and product analysis.

Experimental

Acid Yellow 9 was purchased from Aldrich and was recrystallized from ethanol–water. All other reagents were of reagent grade and were used as supplied. Solutions were freshly prepared in water purified by a Millipore Milli-Q system. For product studies, hydroxyl radicals were generated by γ-radiolysis of water and sulfate radicals were generated by the thermal decomposition of potassium persulfate. Products were separated by either HPLC or TLC analysis. Identification of products was achieved by LC-ESMS analysis of the reaction mixture at different times of reaction and structures of products were confirmed by MS-MS analysis. TLC analyses of reaction mixtures were conducted with silica gel plates using a solvent mixture of ethyl acetate–methanol–25% ammonium hydroxide (6 : 2 : 2 v/v).

HPLC analysis

HPLC analysis of reaction mixtures from sulfate radical and Acid Yellow 9.0 was performed on a Water 600E system equipped with a Waters 994 PDA detector. A Phenomenex@ Nucleosil 5-C18 (250 × 4.60 mm) column was used with a mobile phase consisting of 10 mM of ammonium acetate in methanol and 10 mM of ammonium acetate in water (2 : 8 v/v) running in isocratic mode with a flow rate of 0.6 ml min^{-1}. The detection wavelength was set at 220 nm.

HPLC analysis of reaction mixtures from hydroxyl radicals and Acid Yellow 9, was performed on a Waters LC module 1, using a Waters 996 PDA detector. A Nucleosil C18 (250 × 4.6 mm), 100D column was used for all analytical separations. The mobile phase consisted of 10 mM ammonium acetate in methanol and 10 mM ammonium acetate in water (6 : 4 v/v) running in isocratic mode with a flow rate of 0.7 ml min^{-1}. The detection wavelength was set at 230 nm.

LC-ESMS analysis

LC-ESMS analyses were performed using a Finnigan TSQ 70 mass spectrometer equipped with a Waters 2690 HPLC model and a Waters 2487 dual wavelength detector. A Phenomex Nucleosil 5-C18 (150 × 2 mm) column was used with a mobile phase consisting of 10 mM of ammonium acetate in methanol and 10 mM of ammonium acetate in water (2 : 8 v/v) running in isocratic mode with a flow rate of 0.2 ml min^{-1}. The detection wavelength was set at 220 nm.

Pulse radiolysis

Pulse radiolysis experiments were performed utilizing 2 ns pulses of 8 MeV electrons from a Model Titan Beta-8/16-1S electron linear accelerator.[8] The *G* value denotes the number of species generated per 100 eV, or the approximate micromolar concentration per 10 J of absorbed energy. The radical concentration generated per pulse amounts to (1–3) × 10^{-6} M for

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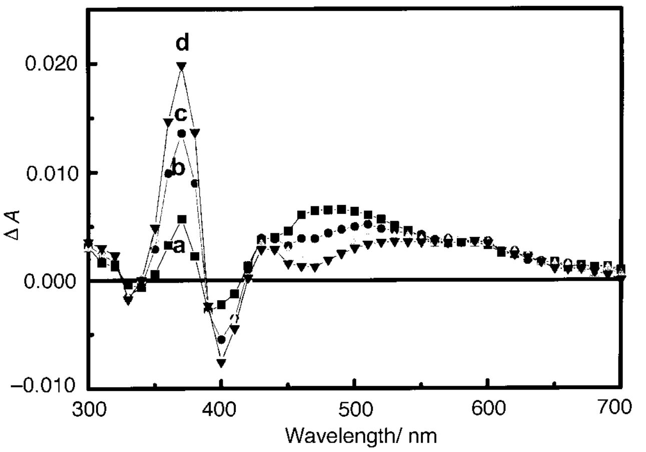


Fig. 1 Time resolved absorption spectra obtained on pulse radiolysis of N_2-saturated aqueous solution of 10^{-4} M Acid Yellow 9, 10^{-2} M $K_2S_2O_8$ and 0.1 M 2-methylpropan-2-ol at pH 7. Spectra were recorded at (a) 2; (b) 5; (c) 8 and (d) 16 μs. pH of the solution was adjusted using 10^{-3} M phosphate buffer.

all the systems investigated in this study. The solutions were saturated with nitrogen or N_2O and flowed continuously through the sample cell during radiolysis.

Radiolysis of dilute aqueous solutions by high-energy electrons and γ-rays leads to the generation of reactive species such as aqueous electrons, $OH^\bullet$ radicals and $H^\bullet$ atoms. In neutral and alkaline solutions, the $H^\bullet$ atom formation is negligible [reaction (1)].

$$H_2O \longrightarrow OH^\bullet, H^\bullet, e_{aq}^-, H^+, H_2O_2, H_2 \qquad (1)$$

Sulfate radical anions were generated *via* the reaction of solvated electrons with the persulfate anion [reaction (2)] in N_2 saturated solutions containing 0.01 M potassium persulfate and 0.1 M 2-methylpropan-2-ol.[9] The 2-methylpropan-2-ol scavenges hydroxyl and hydrogen radicals, generating unreactive alcohol radicals in the process.

$$e_{aq}^- + S_2O_8^{2-} \longrightarrow SO_4^{\bullet -} + SO_4^{2-} \qquad (2)$$

For studying the reaction of hydroxyl radicals, N_2O saturated solutions were used, in which the reaction of solvated electrons with N_2O leads to further generation of hydroxyl radicals [reaction (3)].

$$e_{aq}^- + N_2O + H_2O \longrightarrow N_2 + OH^\bullet + OH^- \qquad (3)$$

γ-Radiolyses of N_2O saturated aqueous samples were performed in a Shepard-109, ^{60}Co source. This is a concentric well type source delivering a dose of 69 Gy min^{-1}. The dose rate of γ-radiation was determined by Fricke dosimetry.[10]

Results

A Pulse radiolysis

Reaction of sulfate radical anions with Acid Yellow 9. Sulfate radical anions react at diffusion-controlled rates [$k = 1.0\ (\pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$] with Acid Yellow 9. Fig. 1 shows the transient absorption spectra at various times following pulse radiolysis of N_2 saturated solutions of Acid Yellow 9 containing potassium persulfate and 2-methylpropan-2-ol at pH 7. Reaction of sulfate radical anions with the dye leads to the formation of a transient with absorption maximum around 490 nm (Fig. 1, curve a). At longer times, the transient absorption around 490 nm exhibits a partial decay which can be fitted to first order kinetics. This transient decay at 490 nm is accompanied by a growth in transient absorption at 370 nm (Fig. 2).

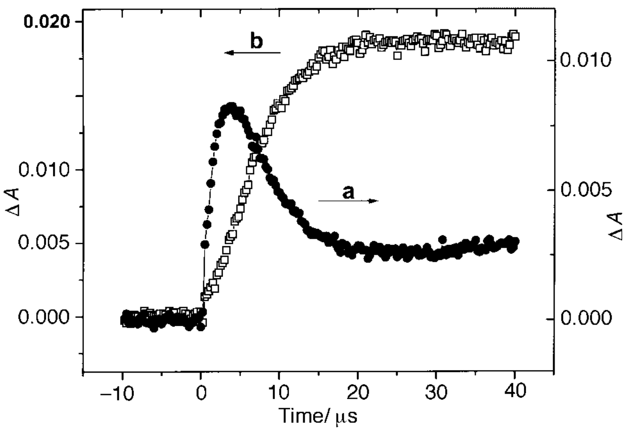


Fig. 2 Transient absorption profile at (a) 500 nm and (b) 370 nm, obtained on pulse radiolysis of N_2-saturated aqueous solution 10^{-4} M Acid Yellow 9, 10^{-2} M $K_2S_2O_8$ and 0.1 M 2-methylpropan-2-ol at pH 7. pH of the solution was adjusted using 10^{-3} M phosphate buffer.

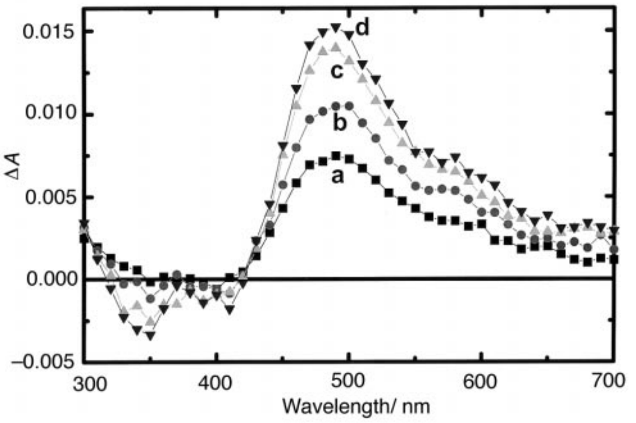


Fig. 3 Time resolved absorption spectra obtained on pulse radiolysis of N_2-saturated aqueous solution of 10^{-4} M Acid Yellow 9, 10^{-2} M $K_2S_2O_8$ and 0.1 M 2-methylpropan-2-ol at pH 4, recorded at (a) 1; (b) 2; (c) 5 and (d) 8 μs.

The sulfate radical anion is a strong one-electron oxidant and can react with the dye to generate the dye radical cation as shown in reaction (4). The transformation of the transient absorption at longer times in Fig. 2 is attributed to the deprotonation of dye radical cation. This aspect was checked by changing the pH of the medium to pH 4. Fig. 3 shows the transient absorption spectrum obtained at pH 4. Under these conditions, the dye radical cation is stable and exhibits an absorption maximum around 490 nm. Moreover, it does not show the first order decay as observed at pH 7. This is indicative of the stability of the dye radical cation at pH 4.

$$Dye + SO_4^{\bullet -} \longrightarrow Dye^{\bullet +} + SO_4^{2-} \qquad (4)$$

In order to confirm the protonation equilibrium the dependence of transient absorption on pH was investigated. The changes in transient absorption intensity as a function of pH were monitored at 370 and 490 nm. The 370 nm transient absorption increases whereas the 490 nm transient absorption decreases with increasing pH (Fig. 4). These results confirm a pH dependent equilibrium between the two transient species with a pK_a of 5.5.

Reaction of hydroxyl radicals with Acid Yellow 9. Fig. 5A shows the transient absorption spectrum observed in the reaction of hydroxyl radicals with Acid Yellow 9 at pH 4. The transient spectrum shows a maximum around 520 nm and depletion in the region of 340–440 nm where the ground state of the dye has a strong absorption. A similar transient absorp-

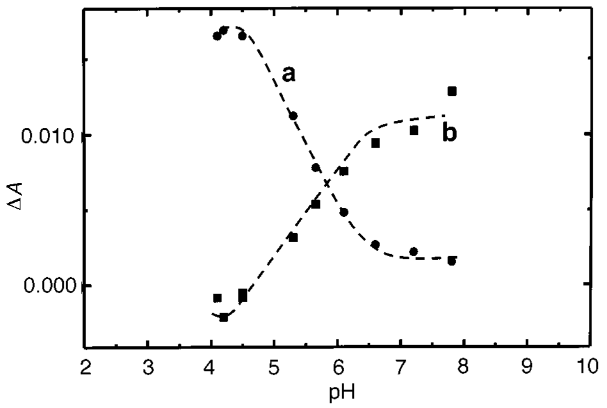


Fig. 4 Dependence of transient absorption at (a) 490 and (b) 370 nm obtained on pulse radiolysis of N_2-saturated aqueous solution 10^{-4} M Acid Yellow 9, 10^{-2} M $K_2S_2O_8$ and 0.1 M 2-methylpropan-2-ol.

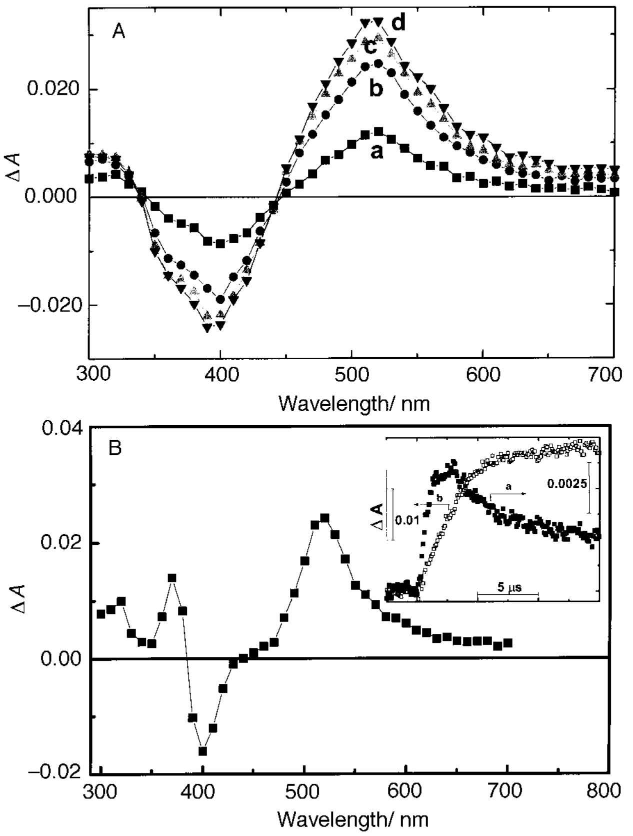


Fig. 5 (A) Time resolved absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of 10^{-4} M Acid Yellow 9 at pH 4 recorded at (a) 0.6; (b) 1.6; (c) 2.6 and (d) 7.1 μs. (B) Time resolved absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of 10^{-4} M Acid Yellow 9 at pH 7 recorded at 13.1 μs. The inset shows transient absorption profile at (a) 480 nm and (b) 370 nm.

tion spectrum is observed in the reaction of hydroxyl radicals with the dye at pH 10. At longer times, a partial decay is observed in the 480 nm region (absorption due to dye cation radical, see Fig. 3) along with a growth in transient absorption in the 360 nm region. The changes observed at these wavelengths are smaller than the corresponding changes observed in the reaction of sulfate radical anions with the dye. The residual transient spectrum obtained after the completion of the first order process possesses a strong absorption in the 520 nm region, unlike in the reaction with sulfate radical anions (Fig. 5B). These observations indicate that in the reaction of hydroxyl radicals with the dye, both hydroxyl adduct formation and electron transfer processes are involved.

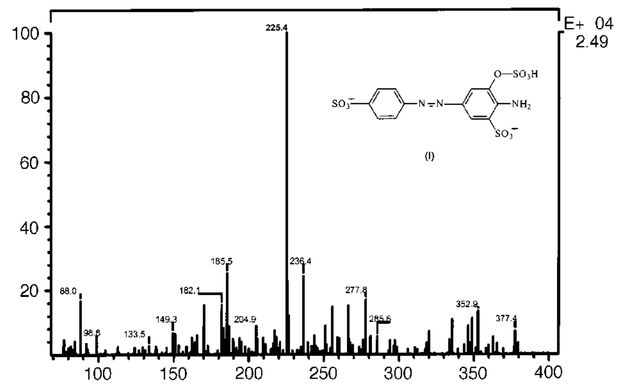


Fig. 6 Mass spectrum of the product mixture from the reaction of sulfate radical anions with Acid Yellow 9.0 at pH 3. The sulfate radical anion was generated by the thermal decomposition of $K_2S_2O_8$ (15 mM) at 65 °C in presence of Acid Yellow 9.0 (10 mM).

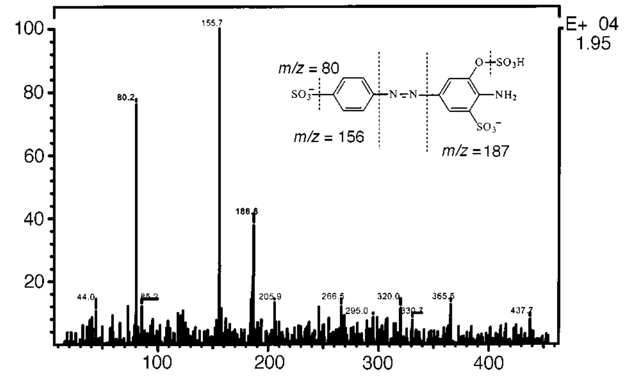


Fig. 7 MS-MS spectrum of the parent ion *m*/*z* = 225.4.

B Product analysis

Reaction of sulfate radical with Acid Yellow 9.0. Reaction of 10 mM Acid Yellow 9 with 1.5 equivalents of $K_2S_2O_8$ at 65 °C, pH ~ 3 gave a mixture of brownish products. Components of the reaction mixture were separated by TLC on silica gel using a solvent mixture of ethyl acetate–methanol–25% ammonium hydroxide (6 : 2 : 2 v/v).

Reaction product **1** (Chart 1) was purified by preparative TLC and its structure elucidated by electrospray mass spectral (ESMS) analysis in the negative ion mode. Product **1** gave a parent ion of *m*/*z* 225.4 which corresponds to a sulfated adduct of Acid Yellow 9 (see Fig. 6 for MS). MS-MS was performed on the parent ion *m*/*z* = 225.4 to obtain structural information. Fig. 7 shows the MS-MS spectrum of *m*/*z* = 225.4 which gave rise to three peaks *m*/*z* = 80, 156 and 187 at 30 eV collisional energy used. These characteristic peaks correspond to loss of SO^{3-}, benzenesulfonate and hydroxyaminobenzenesulfonate. These fragmentations confirmed product **1** as the sulfated adduct of Acid Yellow 9.

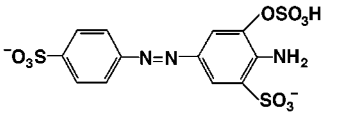


Chart 1 Sulfated adduct of Acid Yellow 9 (**1**).

The same reaction products were observed at a lower concentration of azo dye (1 mM) and persulfate (5 mM). Addition of 100 mM of formate as a radical scavenger leads to a reduction in the yield of the sulfated product. Attempts to identify the products in the brownish mixture by MS were unsuccessful.

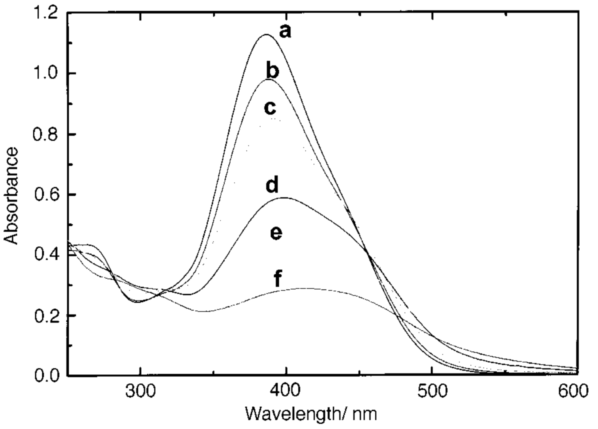


Fig. 8 Dependence of the UV–VIS absorption spectrum of an irradiation time on γ-radiolysis of an N_2O-saturated aqueous solution of 5 mM Acid Yellow 9. Time of irradiation (a) 0; (b) 5; (c) 15 (d) 40; (e) 60 and (f) 90 minutes.

Reaction of hydroxyl radical with Acid Yellow 9.0. γ-Radiolysis of a 0.5 mM solution of Acid Yellow 9.0 at its natural pH (~4.0), saturated with N_2O showed that there is significant dye degradation in 60 minutes. The disappearance of the dye as monitored by its UV–visible absorption at 400 nm (Fig. 8) showed that 80% of the dye is degraded on 60 minutes of irradiation. Reaction mixtures of different irradiation times were analyzed by HPLC and electrospray mass spectroscopy (ESMS). The HPLC of the reaction mixtures at 15, 40 and 60 minutes of irradiation showed the presence of 4 new peaks one of which eluted after the dye. In the sample irradiated at 90 minutes, two additional products were observed which eluted after the dye. These could be high molecular weight coupling products arising from the reaction of initially formed dye radical species.

Electrospray mass spectra of the reaction mixtures showed four major ions with *m*/*z* values of 172.5, 189, 372.5 and (M − 2H)/2 values of 186 and 194 in the negative ion mode. These four peaks were assigned to the products **2**–**5** shown in Chart 2. All these products were further characterized by MS-MS analysis of the individual ions. Characteristic ions at *m*/*z* 80 (loss of SO_3^-) *m*/*z* 156 (loss of benzenesulfonate) and *m*/*z* 187 (loss of hydroxyaminobenzenesulfonate) were observed in the MS-MS of the ion at 186. Similarly for the parent ion *m*/*z* = 194, the fragmentation pattern showed loss of SO_3^- (*m*/*z* 80) hydroxybenzenesulfonate (*m*/*z* = 172) and hydroxyaminobenzenesulfonate (*m*/*z* = 187). Thus the MS-MS analysis confirmed the ions at *m*/*z* 186 and 194 as the hydroxylated (**4**) and dihydroxylated (**5**) dyes respectively.

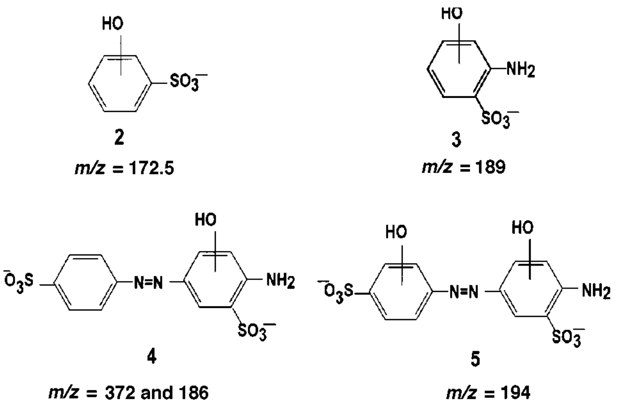
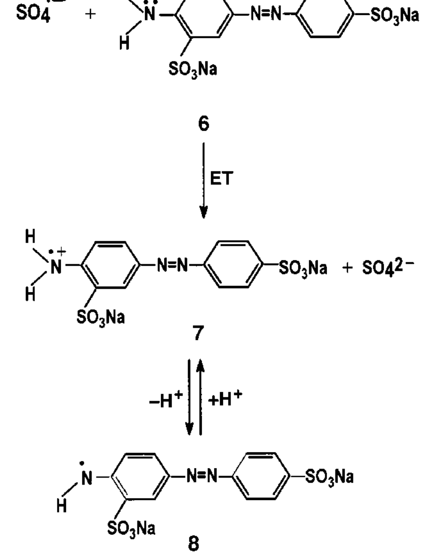


Chart 2

Discussion

In the one electron oxidation of Acid Yellow 9, the electron transfer would most likely occur from the anilino moiety, because of the electron rich nature of this group. The primary steps in the oxidation of the dye are thus expected to be very similar to those observed in one electron oxidation of anilines. The oxidation reaction of anilines has been investigated earlier by several research groups using pulse radiolysis, flash photolysis and by electrochemical methods.[11–15] One electron transfer of anilines leads to the formation of the anilino radical cation, which has a strong absorption, with a maximum at 460 nm. In the present study the reaction of $SO_4^{\bullet -}$ with the dye initially leads to a transient species that has a strong absorption with the maximum at 490 nm. This transient absorption which is stronger and more stable in acidic solutions (pH ~ 4) can be attributed to the radical cation **7** shown in Scheme 1. The red shift in the absorption maximum of the cation radical compared to that of the anilino radical cation reported earlier for simple anilines can be attributed to its conjugation with the azophenyl moiety.

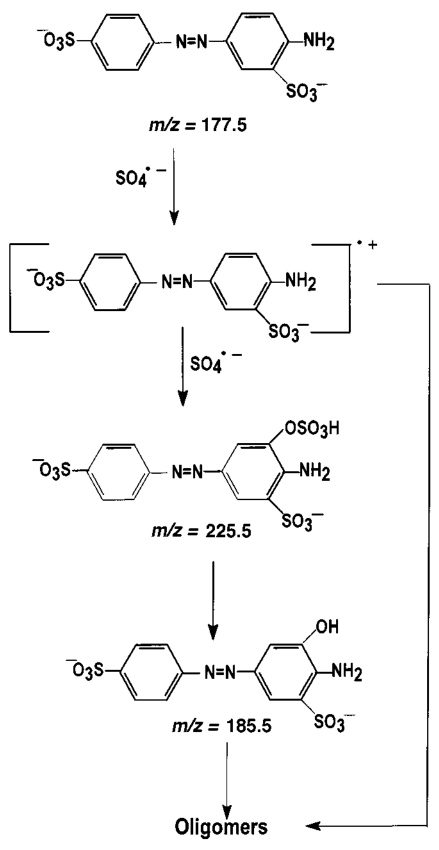


Scheme 1

Deprotonation of the dye radical cation yields the nitrogen-centered anilino radical **8** shown in Scheme 1. The pH dependent decay of the transient absorption around 490 nm and the concomitant growth of transient absorption in the 370 nm can be attributed to the deprotonation step. It may be noted that these changes are comparable to those observed for simpler anilines.[11–15] The radical cation of dimethylaniline, for example, has a strong band centered on 466 nm and the deprotonated aminyl radical has a strong absorption in the 330 nm region.[11]

A major product isolated in the reaction of sulfate radical anions with Acid Yellow 9 was the sulfated product (**1**). This product could arise from the reaction of the dye radical cation with sulfate radicals as shown in Scheme 2. In the product analysis studies, there was also an indication of the formation of high molecular weight compounds, which are likely to be formed by the coupling reactions of the aminyl radicals.

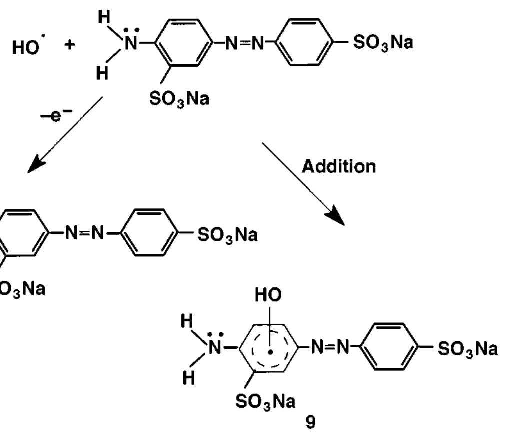
Pulse radiolysis studies of the reaction of hydroxyl radicals with Acid Yellow 9 are indicative of both electron transfer as well as adduct formation. In basic solutions a first-order decay of the 480 nm transient absorption accompanied by a growth in the transient absorption in the 370 nm region (insert Fig. 5B) is observed. This is suggestive of the formation of the dye radical cation, which subsequently undergoes deprotonation. The



Scheme 2

extent of dye radical cation formation in the hydroxyl radical reaction is significantly lesser than that in the reaction of sulfate radicals. Comparison of the transient spectra recorded at pH 4 and 10 (Fig. 5A and B) indicates a strong absorption in the 520 nm region which is unaffected by the pH of the solution. This transient can be attributed to the hydroxyl radical adduct.

Product analysis studies also confirm the hydroxyl radical adduct formation. Four major products namely, the monohydroxylated dye, the dihydroxylated dye, hydroxyaminobenzenesulfonate and hydroxybenzenesulfonate were obtained in the reaction of hydroxyl radical with Acid Yellow 9. The transient absorption centered around 520 nm can be attributed to the radical **9** (Scheme 3). The initial hydroxyl radical adduct formation is suspected to be the one which the OH on the amine bearing phenyl group due to the electrophilic nature of the hydroxyl radical. This is supported by the product analysis study, which yields a monohydroxylated dye product, bearing the hydroxyl group on the benzene ring containing the amine moiety.



Scheme 3

Acknowledgements

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