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One-Electron Oxidation and Reduction of Different Tautomeric Forms of Azo Dyes: A Pulse Radiolysis Study

Kiran K. Sharma,[†,‡] Peter O'Neill,*[,†] John Oakes,[§,||] Stephen N. Batchelor,[§] and B. S. Madhava Rao[‡]

Radiation and Genome Stability Unit, MRC, Harwell, Didcot, Oxfordshire OX11 0RD, U.K., National Centre for Free Radical Research, Department of Chemistry, University of Pune. Pune 411 007, India, and Unilever Research Port Sunlight, Quarry Road East, Bebbington, Wirral, Merseyside CH63 3JW, U.K.

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To characterize the relative reactivities of different dye tautomeric forms of model azo dyes, pulse radiolysis studies were made of their reactions with either oxidizing radicals (hydroxyl radical ($^\bullet$OH) and $N_3^\bullet$) or reducing species (e_{aq}^- and the 2-hydroxy-2-propyl radical) in the pH range 3−12. Methyl orange, 2-(arylazo)-1-naphthol-3,6-disulfonate, and orange I or its O-methylated derivative undergo direct one-electron oxidation with $N_3^\bullet$ and one-electron reduction with either e_{aq}^- or the 2-hydroxy-2-propyl radical. The efficiency of one-electron oxidation of the dyes is strongly dependent upon their different tautomeric forms in the order common ion > hydrazone > azo. In contrast, the ease of reduction of the different tautomeric forms of the dyes is in the order protonated azo ≥ hydrazone > azo > common ion but shows a weaker dependence than that seen for oxidation. Radical intermediates formed either from one-electron oxidation or from one-electron reduction of the dyes mainly decay bimolecularly to give product(s) through radical−radical disproportionation. The reactivity of the $^\bullet$OH is independent of the tautomeric forms of the dyes, forming $^\bullet$OH adducts that decay bimolecularly to give addition product(s) by radical−radical combination (dimerization) at high radical concentrations. However, intermediates formed from orange I and its O-methylated derivative exhibit a competing hydroxyl ion elimination to give the one-electron-oxidized species, which decay by disproportionation, a less efficient process than bimolecular dimerization. Thus, the efficiency of removal of the dye by the $^\bullet$OH is critically dependent on the pH, which governs the competition between the bimolecular dimerization of the $^\bullet$OH adducts and the first-order water elimination pathway.

Introduction

The oxidation/reduction of azo dyes has drawn much attention because of the commercial and in particular environmental concerns over residual dyes present in waste streams.[1,2] Therefore, one of the major areas of interest in dye chemistry is to look for an efficient way for the disposal and treatment of wastewater by oxidation/reduction processes. Whereas advances to their molecular design have improved their photostability and stability toward aerobic degradation or common oxidants, their chemical removal is extremely difficult. This has stimulated the development of advanced photochemical methods, like photo-Fenton reaction[3a,b] and photocatalytic reaction with suspended semiconductors[4a,b] such as TiO_2 to remove dyes. Decolorization of the dyes by the sonochemical method[5a,b] has also been used. All these methods, however, involve the production of a reactive free radical species such as hydroxyl radicals ($^\bullet$OH), which interact with the dyes leading to the decomposition of the dyes. Recently, it has been shown that reducing radicals are very effective at bleaching azo dyes.[6a,b]

If the azo group is conjugated with hydroxy groups, the dyes exist in different tautomeric forms (Scheme 1). Consequently, it is difficult not only to interpret the structure−reactivity relationship but also to identify and characterize the intermediate species involved so that a plausible mechanism(s) may be proposed for decolorization of the dyes. Our previous study[7] using a series of azo dyes based on 1-(arylazo)-2-naphthol-6-sulfonate (I) showed that these dyes undergo free radical-induced oxidation and reduction processes leading to decolorization of the dyes. Furthermore, the $^\bullet$OH adduct of I was most efficiently discolored by bimolecular processes involving radical−radical combination (dimerization), rather than by a dehydration process, commonly observed with phenolic materials, to give a radical corresponding to that produced by one-electron oxidation. For instance, $^\bullet$OH-induced degradation of the azo dyes at pH ∼7, where the dyes are predominantly in their hydrazone form (see Scheme 1), is more efficient when compared with that induced by e^-_{aq} or one-electron oxidation. The reduction properties of the one-electron-oxidized dye radical of the common ion form[8] of some azo dyes are known.

The main objectives of this investigation were to characterize the relative reactivities of the azo, hydrazone, and common anion tautomers of a series of azo dyes with one-electron reducing and oxidizing agents at different pH values. For comparison with methods used in decolorization of the dyes, the reaction of these dyes with $^\bullet$OH was also investigated. Because the pK_a value of the model azo dye I is ≥11 and similar to the pK_a values of the $^\bullet$OH[9] and 2-hydroxy-2-propyl radicals,[10a] azo dyes based on orange I (II), which have lower pK_a values, were chosen,[11,12] to minimize any possible differences in reactivity

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* Corresponding author. Tel: ++44 1235 841017. Fax: ++44 1235 841200. E-mail: p.oneill@har.mrc.ac.uk.

[†] MRC.

[‡] University of Pune.

[§] Unilever Research Port Sunlight.

[||] Freelance Consultant, John Oakes Associates Farm Bungalow, Darnhall School Lane, Winsford, Cheshire CW7 1LH, U.K. E-mail: John@OakesAssociates.Freeserve.co.uk.

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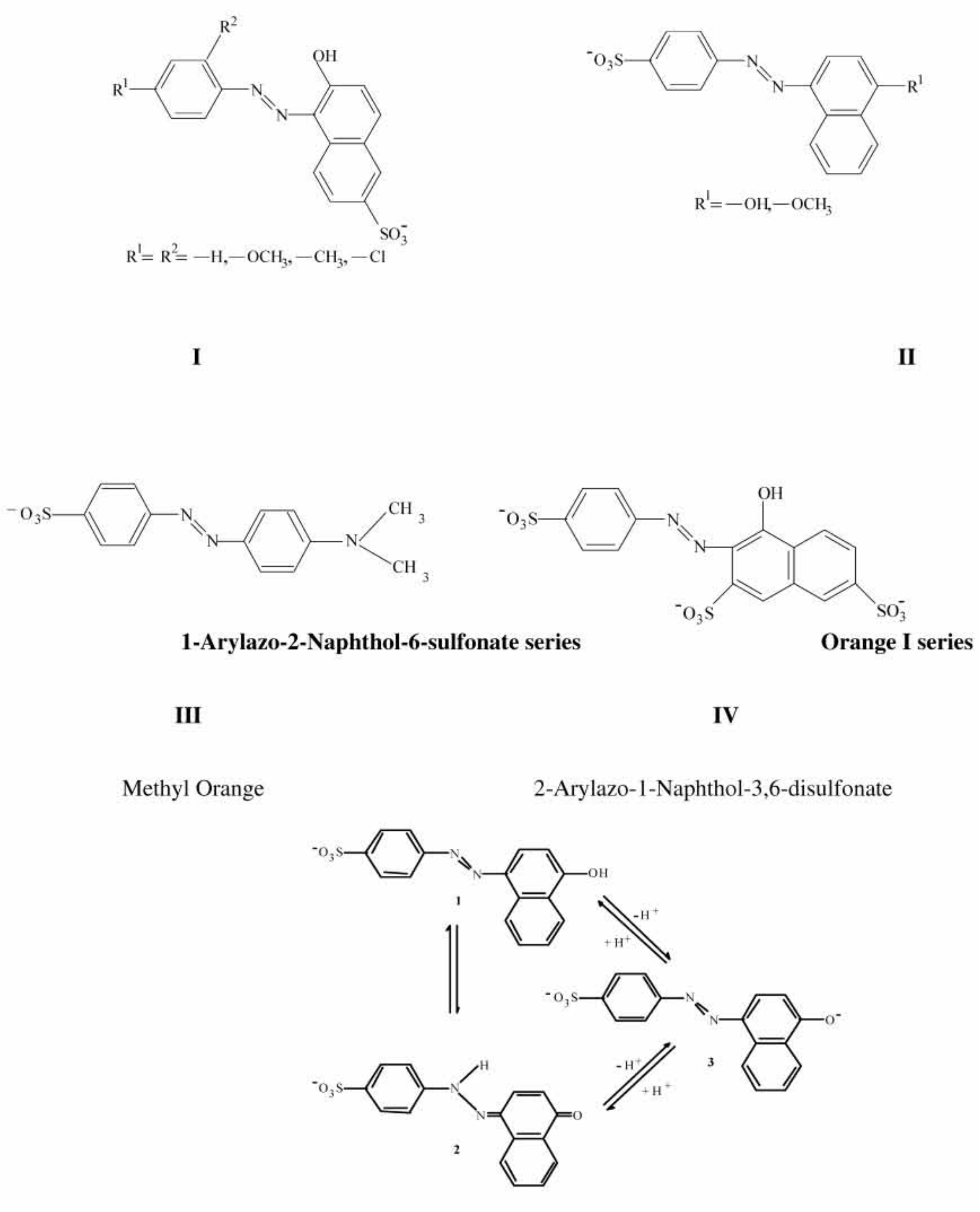
SCHEME 1: Azo (1), Hydrazone (2), and Common Anion (3) Forms of Orange I



reflecting the different forms of these initiating radicals or electrostatic effects when e^-_{aq} is used. Orange I (II) with pK_a 8.3 was chosen to study the reactivities of the azo/hydrazone and common ion tautomers whereas O-methylated orange I (II) and methyl orange (III) were used as models of the fixed azo tautomer and to gain insight into the effects of different electron-donating groups on the chemistry of oxidation between orange I and methyl orange. 2-(Arylazo)-1-naphthol-3,6-disulfonate (IV) was used for comparison with previous data[7] with 1-(arylazo)-2-naphthol-6-sulfonate using azo dyes with various substituents.

Experimental Section

Orange I (Fluka) and methyl orange (Aldrich) were recrystallized in ethanol−water before use. The synthesis, purification, characterization, and properties of 2-(arylazo)-1-naphthol-3,6-disulfonate (sodium salt) have been described elsewhere.[13] O-methylated orange I was used as supplied by Peter Gregory (Zeneca) and Richard Clark, Unilever Port Sunlight Laboratory. *N*,*N*,*N*′,*N*′-Tetramethyl-1,4-phenylenediamine (TMPD) and 7,8-dihydrodipyrido[1,2-*a*:2′,1′-*c*][1,4]diazepinedium ($3V^{2+}$) were obtained from Aldrich, 2,2′-azinobis(3-ethyl)[1,3]benzothiazoline-6-sulfonic acid (ABTS) was from Boehringer Ltd., and all other chemicals were from Aldrich and Sigma and used as supplied. Solutions were freshly prepared in phosphate buffer (1×10^{-3} mol dm^{-3}) using water purified by a Millipore Milli-Q system. The pH of the solutions was adjusted using either AR grade $HClO_4$ or NaOH. Ground state optical absorption spectra of the dyes were recorded immediately prior to irradiation using a Beckman DU 7400 spectrophotometer. A syringe-bubbling technique was used to saturate the solutions with the appropriate gas (either high-purity N_2O, BOC special gas, or N_2 Air Products). The solutions were bubbled for 20 min prior to irradiation. All the experiments were carried out at room temperature (~20 °C).

Pulse radiolysis experiments were carried out using a 4.3 MeV Mullard Linear Accelerator, SL46, which generates single electron pulses of 1.6 μs duration. Spectrophotometric detection of the transient dye radicals produced was monitored as described previously.[7,14] Signals from the photomultiplier were stored using a Datalab transient digitizer (model DL 905) interfaced with a PC 386/20, which utilizes a customized version of ASYST software (Technologies Inc.) to process the data. Appropriate glass filters and a shutter were used to minimize the effects of photolysis of the samples. KSCN dosimetry was carried out to determine the dose/pulse using aqueous solutions containing 1×10^{-4} mol dm^{-3} KSCN and taking $G\epsilon^{500\mathrm{nm}} = 2.6 \times 10^{-4}$ m^2 J^{-1} for[15,16] $(\mathrm{SCN})_2^{\bullet-}$. The dose/pulse was in the range 1−10 Gy, which produces at the highest dose a [radical] of $\leq 6 \times 10^{-6}$ mol dm^{-3}. The accuracy of the rate constants determined for the reactions of $^\bullet$OH, $N_3^\bullet$, and the 2-hydroxy-2-propyl radical with the dyes is within ±10%.

γ-Irradiation. ^{60}Co-γ-irradiation of aqueous solutions containing azo dye (5×10^{-5} mol dm^{-3}) saturated with the appropriate gas was carried out using a well type ^{60}Co γ-source in the Department of Chemistry, University of Pune, or the facilities at the Radiation and Genome Stability Unit, Medical Research Council. The dose rates were determined using Fricke dosimetry.

Irradiations. Radiolysis of aqueous solution with γ-radiation or highly energetic electrons leads to the generation of highly reactive species (reaction 1), the yields of which are well-known; $G(^\bullet\mathrm{OH}) \sim G(e_{aq}^-) = 2.8 \times 10^{-7}$ mol J^{-1} and $G(\mathrm{H}^\bullet) = 0.55 \times 10^{-7}$ mol J^{-1}.

$$\mathrm{H_2O} \rightsquigarrow {}^\bullet\mathrm{OH}, \mathrm{H}^\bullet, e_{aq}^-, \mathrm{H_2O_2}, \mathrm{H_2}, \mathrm{H_3O^+} \tag{1}$$

e^-_{aq} ($E(\mathrm{H_2O}/e^-_{aq}) = -2.87$ V) may be quantitatively converted into $^\bullet$OH (p$K_a \approx 11.9$)[9] by saturating the aqueous solution with N_2O (reaction 2).

$$e_{aq}^- + \mathrm{N_2O} + \mathrm{H_2O} \rightarrow \mathrm{N_2} + {}^\bullet\mathrm{OH} + \mathrm{OH^-} \tag{2}$$

$$k = 8.7 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7}^9$$

The oxidizing $N_3^\bullet$ radical was generated in N_2O-saturated, aqueous solution containing 2.0×10^{-2} mol dm^{-3} NaN$_3$, where $^\bullet$OH is converted into $N_3^\bullet$ (reaction 3).

$${}^\bullet\mathrm{OH} + \mathrm{N_3^-} \rightarrow \mathrm{N_3^\bullet} + \mathrm{OH^-} \tag{3}$$

$$k = 1.2 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7}^9$$

Solvated electrons are generated under dearated aqueous solution containing 2-methylpropan-2-ol (0.2 mol dm^{-3}) as a scavenger of $^\bullet$OH (reaction 4).

$${}^\bullet\mathrm{OH} + (\mathrm{CH_3})_3\mathrm{COH} \xrightarrow{\mathrm{N_2}} {}^\bullet\mathrm{CH_2C(CH_3)_2OH} + \mathrm{H_2O} \tag{4}$$

$$k = 7.6 \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7}^9$$

2-Hydroxy-2-propyl radicals ($E((\mathrm{CH_3})_2\mathrm{CHOH}/(\mathrm{CH_3})_2\mathrm{C^\bullet{-}OH}) = -1.8$ V, p$K_a \sim 12.2$)[10a] are generated by quantitative conversion of OH radical under N_2O conditions containing 0.1 mol dm^{-3} 2-propanol (reaction 5).

$${}^\bullet\mathrm{OH} + (\mathrm{CH_3})_2\mathrm{HCOH} \xrightarrow{\mathrm{N_2O}} {}^\bullet\mathrm{COH(CH_3)_2} + \mathrm{H_2O} \tag{5}$$

$$k^9 = 1.9 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

$\mathrm{SO_4^{\bullet-}}$ was generated in deaerated, aqueous solutions containing 1.5×10^{-2} mol dm^{-3} Na$_2$S$_2$O$_8$ and 2.0×10^{-2} mol dm^{-3} 2-methylpropan-2-ol, as a scavenger of $^\bullet$OH (reaction 6).

$$\mathrm{S_2O_8^{2-}} + e_{aq}^-\ (^\bullet\mathrm{H}) \rightarrow \mathrm{SO_4^{\bullet-}} + \mathrm{SO_4^{2-}}\ (\mathrm{HSO_4^-}) \tag{6}$$

$$k_{e_{aq}^-} = 1.2 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7}^9$$

$$k_{\mathrm{H}^\bullet} = 2.5 \times 10^7\ \mathrm{dm^3\ mol^{-1}\ s^{-1}\ at\ pH\ 7}^9$$

Ground State Correction. Because the ground state of the dyes absorbs very strongly in the visible, the transient optical absorbance of the radicals at a given wavelength was characterized by using eq 7 to determine the extinction coefficients of the radicals ($\epsilon_{\mathrm{radical}}$). Equation 7 accounts for bleaching of the reacted parent compound after irradiation and uses the molar absorptivity of the parent compound ($\epsilon_{\mathrm{parent}}$) and the absorbed dose to calculate $\epsilon_{(\mathrm{radical})}$ using the optical absorbance determined at the wavelength investigated (OD$_{\mathrm{measured}}$).

$$\epsilon_{\mathrm{radical}} = \epsilon_{\mathrm{parent}} + \frac{\mathrm{OD_{measured}}(G\epsilon^{\lambda})_{\mathrm{dosimeter}}}{G_{\mathrm{radical}}(\mathrm{OD}^{\lambda})_{\mathrm{dosimeter}}} \tag{7}$$

Determination of One-Electron Reduction Potentials. The one-electron reduction potentials ($\mathrm{D^{\bullet+}/D}$) of the one-electron-oxidized radical of orange I (D) at pH 7 and 10 were determined pulse radiolytically in aqueous solution containing 2.0×10^{-2} mol dm^{-3} of sodium azide to maintain an oxidizing system (reaction 9). The yield of radicals shown in reaction 9 was determined at equilibrium[17,18] using *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine (TMPD) as the standard, the reduction potential of which ($\mathrm{TMPD^{\bullet+}/TMPD}$) is 0.35 V [19] vs NHE. The nonequilibrium mixture of one-electron-oxidized radicals of orange I and TMPD were generated following pulse irradiation of aqueous solutions containing 1×10^{-3} mol dm^{-3} orange I and various concentrations of TMPD [$(0.05-0.7) \times 10^{-3}$ mol dm^{-3}] with a dose/pulse of ~1 Gy.

$$\mathrm{D^{\bullet+}/D^\bullet} + \mathrm{TMPD} \rightleftharpoons \mathrm{D/D^-} + \mathrm{TMPD^{\bullet+}} \tag{8}$$

The position of equilibrium (9) was determined from the concentration of $\mathrm{TMPD^{\bullet+}}$ at 610 nm, as the absorbance of the one-electron-oxidized dye radical ($\mathrm{D^{\bullet+}}$) is negligible compared with that of $\mathrm{TMPD^{\bullet+}}$ at 610 nm.

Similarly, the one-electron reduction potential for methyl orange at pH 7.0 was determined using $3\mathrm{V^{2+}}$ ($E(3\mathrm{V^{2+}}/3\mathrm{V^{\bullet+}}) = -0.549$ V)[19] as the standard. The position of equilibrium (10) was determined from the absorbance of $3\mathrm{V^{\bullet+}}$ at 380 nm using a dose/pulse of ~4 Gy.

$$e_{aq}^-(\mathrm{CO_2^{\bullet-}}) + \mathrm{MO} \rightarrow \mathrm{MO^{\bullet-}} + \mathrm{HCO_2} + \mathrm{OH^-} \tag{9}$$

$$\mathrm{MO^{\bullet-}} + 3\mathrm{V^{2+}} \rightleftharpoons \mathrm{MO} + 3\mathrm{V^{\bullet+}} \tag{10}$$

The aqueous solutions contained 0.1 mol dm^{-3} formate, to maintain a reducing system, 1×10^{-4} mol dm^{-3} methyl orange dye, and various concentrations of $3\mathrm{V^{2+}}$ [$(1-10) \times 10^{-5}$ mol dm^{-3}]. The equilibria (8) and (10) can be related to the concentrations of the substrate radicals, using the system

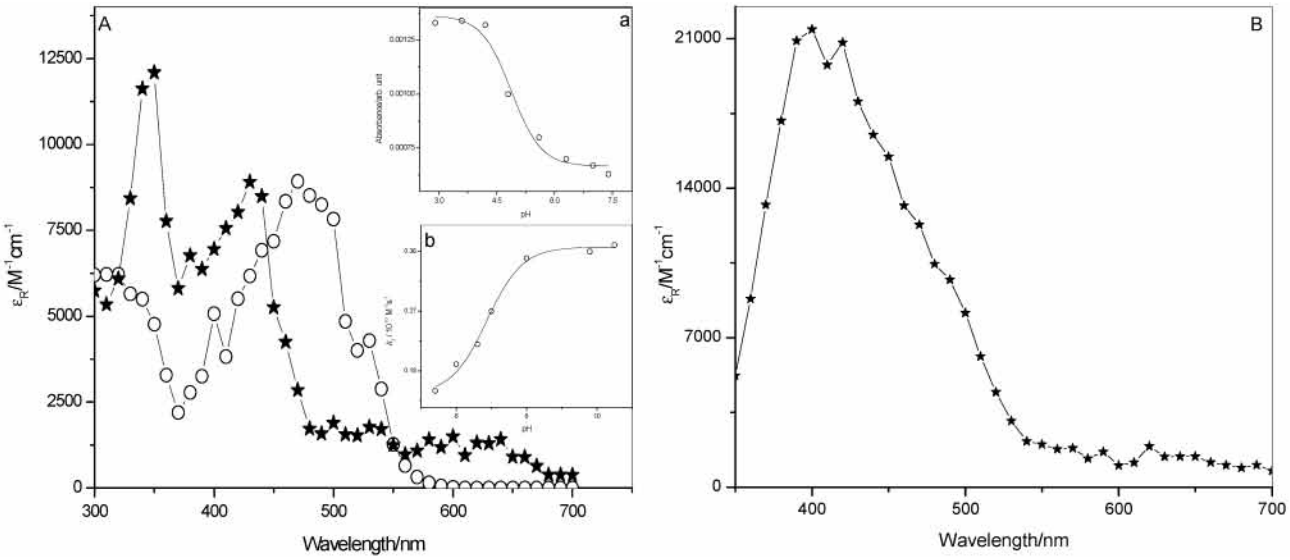


Figure 1. Corrected transient optical absorption spectra obtained in the reaction of (A) $N_3^•$ (★, 30 μs after pulse irradiation) at pH 6.6 and $SO_4^{•-}$ (○, 20 μs after pulse irradiation) with orange I at pH 4.0 and (B) $N_3^•$ with methyl orange (★, 30 μs after pulse irradiation) at pH 7.0. Insets: (a) dependence of the optical absorbance of the radical at 380 nm on pH for reaction of $SO_4^{•-}$ with orange I; (b) dependence of the second-order rate constant for the reaction of $N_3^•$ with orange I on pH. [Dye] = 5×10^{-5} mol dm^{-3}. Dose/pulse = 2 Gy.

containing $3V^{•+}$ as the example, and the ratio of the (substrate D):(standard $3V^{•+}$) using

$$K = \frac{[D][OD_{obs} - OD_{D^{•-}}]}{[A][OD_{3V^{•+}} - OD_{obs}]} \qquad (11)$$

The equilibrium constant (K) is related to the difference in the reduction potentials (ΔE) of the reactants in

$$\Delta E = E(D/D^{•-}) - E(3V^{•+}/3V^{•+}) = RT \ln K/F \qquad (12)$$

where F is the Faraday constant. Thus the one-electron reduction potentials can be calculated. The potentials are corrected for the ionic strength as described in detail elsewhere.[19]

Results and Discussion

(a) Rate Constants for Reaction of $^•$OH, $N_3^•$, and the 2-Hydroxy-2-propyl Radical with the Dyes. The rate constants for the reaction of $^•$OH, the oxidizing $N_3^•$, and the reducing 2-hydroxy-2-propyl radical with orange I, O-methylated orange I, methyl orange, and 2-(arylazo)-1-naphthol-3,6-disulfonate were determined in aqueous solutions at different pH values. The second-order rate constants were evaluated from the linear dependence of the first-order rate of growth of the transient optical absorption on the concentration of the dyes [$(0.1-1) \times 10^{-4}$ mol dm^{-3}] and are tabulated in Table 1 along with the corresponding second order rate constants for 1-(arylazo)-2-naphthol-6-sulfonate dye series previously reported.[7]

The rate constants for reaction with $^•$OH are similar to the rate constants previously determined for reaction of $^•$OH with 1-(arylazo)-2-naphthol-6-sulfonate[7] and azobenzene.[20] The rate constants with $^•$OH show very little variation with the tautomeric form of the dyes, because they react at the diffusion-controlled limit, which, to a first approximation, is given by the Stokes–Einstein equation, $k_d = 8RT/3\epsilon = 7 \times 10^9$ dm^3 mol^{-1} s^{-1}. In contrast, the rate constants for reaction of both $N_3^•$ and the 2-hydroxy-2-propyl radical with these dyes depend strongly on the tautomeric forms of the dyes.

TABLE 1: Second-Order Rate Constants (k/10^{10} dm^3 mol^{-1} s^{-1}) for the Reaction of $^•$ OH, $N_3^•$, and the 2-Hydroxy-2-propyl Radical with Orange I, O-Methylated Orange I, Methyl Orange, 2-(Arylazo)-1-naphthol, and 1-(Arylazo)-2-naphthol Dyes

dyes	pK_a	pH	$^•$OH k	$N_3^•$ k	$^•$COH(CH$_3$)$_2$ k
		3.0	nd		0.3
orange I	8.3	4.0	0.7		nd
(II)		5.4	nd	0.15	0.23
		6.4	nd	0.19	0.2
		6.6	0.9	0.22	0.18
		7.0	nd	0.26	0.15
		8.0	nd	0.35	0.07
		9.0	nd	0.37	nd
		10.5	1.1	0.4	0.04
O-methylated orange I	3.4	7.0	1.1	≤0.01	0.08
(fixed azo; II)					
methyl orange		3.2	nd		0.2
(fixed azo; III)		7.0	nd	0.5	0.07
		9.6	2.0[27]	nd	0.06
2-(arylazo)-1-naphthol	11.3	7.0	1.8	≤0.01	0.2
(IV)		12.3		0.4	nd
1-(arylazo)-2-naphthol[7]					
(I)					
$R^1 = R^2 = H$	10.8	7.0	1.1	0.07	0.25
		12.0	nd	0.5	nd

[a] nd = not determined; superscripts refer to rate constants taken from indicated literature references (refs 7 and 27).

For instance, the rate constant for reaction of $N_3^•$ with the fixed azo dye, O-methylated orange I, is low, $<1 \times 10^8$ dm^3 mol^{-1} s^{-1}, whereas the rate constant with orange I increases with pH, as shown in Figure 1A (inset b) reaching a value of 3.7×10^9 dm^3 mol^{-1} s^{-1} at pH 10.5, when the dye is present as the common anion. Similarly, the rate constant for reaction of $N_3^•$ with 2-(arylazo)-1-naphthol-3,6-disulfonate at pH 7.0 is low when the dye is present predominantly in its hydrazone form but increases with pH to reach a value of 4×10^9 dm^3 mol^{-1} s^{-1} when the dye is present as its common anion, i.e., when pH > pK_a of the dye. Similar changes of the rate constants with pH were also seen previously[7] for reaction of $N_3^•$ with unsubstituted 1-(arylazo)-2-naphthol-6-sulfonate. Therefore, the efficiency of one-electron oxidation of the different tautomeric forms of the dyes is in the order common ion > hydrazone > azo, consistent with the findings for the oxidation using peracids and hypochlorites,[21] where the common anion is more susceptible to oxidation compared with the other tautomers. The lower

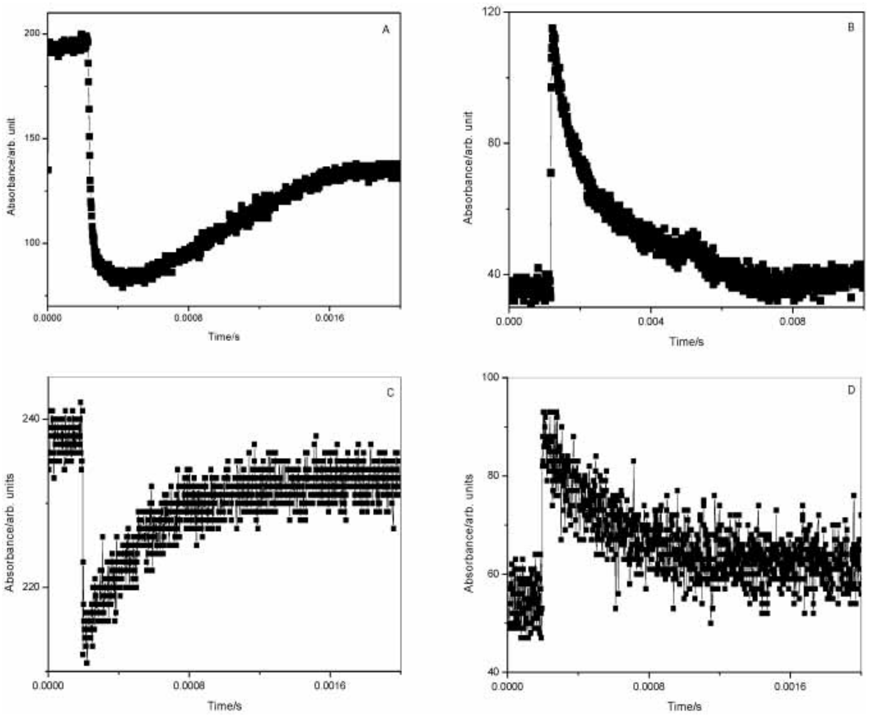


Figure 2. Optical absorbance changes with time determined at pH 6.6 for [dye] of 5×10^{-5} mol dm^{-3} and a dose/pulse = 2 Gy. (A) Optical absorbance changes with time for reaction of $N_3^{\bullet}$ with orange I at 480 nm. (B) Decay of the one-electron-oxidized radical of orange I at 340 nm. (C) Optical absorbance changes with time for reaction of 2-hydroxy-2-propyl radical with orange I at 480 nm. (D) Decay of the electron adduct of orange I at 400 nm.

reactivity of $N_3^{\bullet}$ with 2-(arylazo)-1-naphthol-3,6-disulfonate (IV) compared with 1-(arylazo)-2-naphthol-6-sulfonate (I) at pH 7.0 (when both are predominantly in their hydrazone forms) parallels the reactivities of the respective common anions. The reduction potential of the oxidized common anion[8] of IV (0.84 V) is higher than that of I (~0.7 V) and probably reflects the electron-withdrawing effects of the two additional sulfonate groups of 2-(arylazo)-1-naphthol-3,6-disulfonate. The greater reactivity of orange I with $N_3^{\bullet}$ than either 2-(arylazo)-1-naphthol-3,6-disulfonate or 1-(arylazo)-2-naphthol-6-sulfonate, when in their hydrazone forms, is consistent with their different reduction potentials (see below). Although methyl orange and O-methylated orange I are both in the azo form, the rate constant for oxidation of methyl orange is much greater, reflecting oxidation of the dimethylanilino moiety due to the effect of the strong electron-donating effect of the dimethylamine group into the conjugated π-system.

With the 2-hydroxy-2-propyl radical, its reactivity with orange I and 2-(arylazo)-1-naphthol-3,6-disulfonate also reflect the tautomeric forms of the dyes but to a lesser extent than that seen with $N_3^{\bullet}$. At pH 6−7, when the dyes are present predominantly in the hydrazone form, the rate constants are similar to that for reaction with azobenzene.[22] Interestingly, the rate constant for orange I measured at pH 7 in water is an order of magnitude higher than that found in methanol,[23] indicating a relatively large solvent effect for this reaction. With orange I, the rate constant decreases with increase in pH, as shown in Figure 3 (inset b), indicating that the common ion is less reactive than the hydrazone form. With methyl orange, the azo tautomer present at pH 7.0 and 9.6 is less reactive than the protonated azo[21] form present at pH 3.2 (see Table 1). Therefore, in contrast to oxidation of the dyes, the ease of reduction of the different tautomeric forms of the dyes is in the order protonated azo ≥ hydrazone > azo > common ion.

(b) Species Produced on One-Electron Oxidation of the Dyes by $N_3^{\bullet}$. Because the reactivity of the dyes with $N_3^{\bullet}$ depends on their tautomeric forms, the optical absorption spectra of the species produced on reaction with $N_3^{\bullet}$ at different pH values have been determined. The corrected transient optical absorption spectrum for the species produced in the reaction of $N_3^{\bullet}$ with orange I at pH 6.6, as shown in Figure 1A, is similar to the spectrum of the species produced in the reaction of $N_3^{\bullet}$ with orange I at pH 10, 2-(arylazo)-1-naphthol-3,6-disulfonate at pH 12.4 (Figure 1S), and unsubstituted 1-(arylazo)-2-naphthol-6-sulfonate[8] at pH 12.0. The transient optical absorption spectra are assigned to the one-electron-oxidized radical of the dyes.

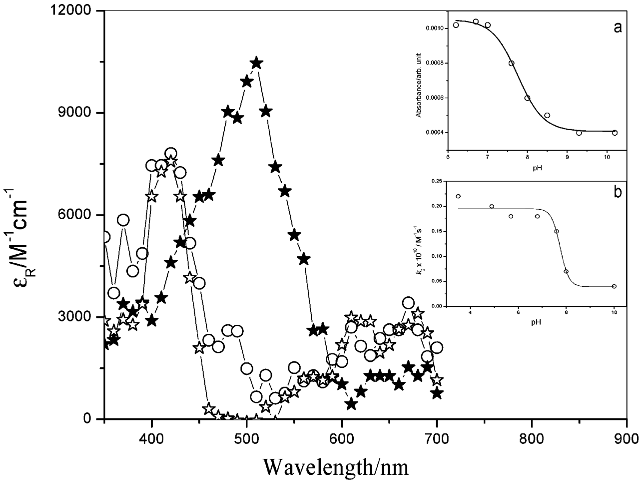


Figure 3. Corrected transient optical absorption spectra of the species formed in the reaction of 2-hydroxy-2-propyl radical (○, 20 μs after the radiation pulse) at pH 6.6 and e_{aq}^- (20 μs, after the radiation pulse, at pH 6.6 (☆) and 10.0 (★)) with orange I. Insets: (a) dependence of the optical absorbance at 410 nm on pH for the reaction of e_{aq}^- with orange I; (b) dependence of the second-order rate constant on pH for the reaction of 2-hydroxy-2-propyl radical with orange I. [Dye] = 5×10^{-5} mol dm^{-3}. Dose/pulse = 2 Gy.

The pK_a of the one-electron-oxidized species of orange I was determined using $SO_4^{\bullet-}$ as the oxidizing agent due to working in acidic conditions because the pK_a of $N_3^{\bullet}$ is 4.74.[10b] First, it was verified that the optical absorption spectrum for reaction of $SO_4^{\bullet-}$ with orange I is identical with that of the one-electron-oxidized species produced with $N_3^{\bullet}$ at pH ~6.6. However, at pH 4.0, the optical absorption spectrum of the species produced in the reaction of $SO_4^{\bullet-}$ with orange I is different, showing a red shift with respect to the absorption maximum at 430 nm (Figure 1A). From the dependence of optical absorbance of the species produced in the reaction of $SO_4^{\bullet-}$ with orange I on pH as shown in inset (a) of Figure 1A, the pK_a of the one-electron-oxidized radical of orange I was determined to be 4.8 ± 0.2, similar to the pK_a of 5.2 ± 0.2 reported[7] for the *p*-methoxy derivative of 1-(arylazo)-2-naphthol-6-sulfonate. With methyl orange, the corrected transient optical absorption spectrum produced in the reaction with $N_3^{\bullet}$ at pH 7.0 (Figure 1B) is assigned to its one-electron-oxidized species. As discussed earlier, the oxidation of methyl orange is suggested to occur at the dimethylanilino moiety, whereas oxidation of the methoxynaphthol moiety of O-methylated orange I is not efficient ($k < 10^8$ dm^3 mol^{-1} s^{-1}).

The one-electron-oxidized radicals of orange I and 2-(arylazo)-1-naphthol-3,6-disulfonate determined at 340−360 nm decay bimolecularly with second-order rate constants (2k) of 2.7×10^9 dm^3 mol^{-1} s^{-1} at pH 6.6 (Figure 2B) and 2×10^9 dm^3 mol^{-1} s^{-1} at pH 7.0, respectively. The value of 1.6×10^{10} dm^3 mol^{-1} s^{-1} appears to be too large. Bimolecular radical termination in water would be expected to have values of less than 2×10^9 dm^3 mol^{-1} s^{-1}, due to spin statistics.[24] Thus, for example, 2-hydroxy-2-propyl radicals decay bimolecularly with a rate constant of 1×10^9 dm^3 mol^{-1} s^{-1} in water.[25] The high value determined in the present study probably reflects a small underestimation of the initial concentration of dye radicals to which this fit is very sensitive. This may also be true for the bimolecular termination constants found for some of the other dye radicals; vide supra. At 390 nm, the radical cation of methyl orange decays exponentially with a first-order rate constant of 1.4×10^3 s^{-1}.

The reduction potential for one-electron-oxidized orange I at pH 7 ($E^1_7(\mathrm{D}^{\bullet+}/\mathrm{D})$) and 10 ($E^1_{10}(\mathrm{D}^{\bullet+}/\mathrm{D})$) were determined to be +0.31 ± 0.01 and +0.35 ± 0.01 V (vs NHE), respectively, after correcting for ionic strength. The reduction potential at pH 10 is lower than the reported[8] values of $E^1_{12}(\mathrm{D}^{\bullet+}/\mathrm{D}) = 0.64-0.76$ V vs NHE for one-electron-oxidized radicals of 1-(arylazo)-2-naphthol-6-sulfonate and derivatives at pH 12 and the value of 0.84 V for the one-electron-oxidized radical of 2-(arylazo)-1-naphthol-3,6-disulfonate using ClO_2 at pH 12.

Attempts were made to determine the reduction potentials of one-electron-oxidized radicals of 1-(arylazo)-2-naphthol-6-sulfonate and 2-(arylazo)-1-naphthol-3,6-disulfonate dyes at pH 7.0 using ABTS ($E^1_7(\mathrm{ABTS}^{\bullet+}/\mathrm{ABTS}) = 0.648$ V)[19] as the standard. However, no equilibrium could be established from which it was estimated that the reduction potentials of their one-electron-oxidized radicals ($\mathrm{D}^{\bullet+}/\mathrm{D}$) are >0.8V.

(c) Species Produced by One-Electron Reduction of the Dyes by the 2-Hydroxy-2-propyl Radical and e_{aq}^-. To characterize the transient species of the different tautomeric forms of the dyes following one-electron reduction, the transient optical absorption spectra were measured for the reaction of e_{aq}^- and the 2-hydroxy-2-propyl radical with the dyes. The corrected transient optical absorption spectra for the species produced in the reaction of e_{aq}^- and the 2-hydroxy-2-propyl radical with orange I at pH 6.6 are similar, as shown in Figure 3. At pH 3.0, the transient optical absorption spectrum produced by the reaction of 2-hydroxy-2-propyl radical with orange I (data not shown) is the same as that observed at pH 6.6, whereas at pH 10 the transient optical absorption spectrum formed by reduction of orange I with e_{aq}^- (Figure 3) or 2-hydroxy-2-propyl radical is red shifted compared with the spectrum at pH 6.6. These transient optical absorption spectra are assigned to one-electron-reduced species of orange I. From the dependence of the optical absorbance at 410 nm for reaction of e_{aq}^- with orange I on pH, the pK_a of the electron adduct of orange I was determined to be 7.9 ± 0.2 (Figure 3, inset a), and similar to that of parent orange I (8.3). It is therefore suggested that the pK_a determined for the one-electron-reduced radical of orange I reflects the prototropic equilibrium of the hydroxyl group.

The corrected transient optical absorption spectrum produced in the reaction of e_{aq}^- and the 2-hydroxy-2-propyl radical with methyl orange at pH 7.0 are similar to each other and to that observed for one-electron reduction of azobenzene.[26] The transient spectrum produced in the reaction of 2-hydroxy-2-propyl radical with methyl orange at pH 3 shows a blue shift with respect to that at pH 7.0 (data not shown); this species arises from reduction of the protonated azo (pK_A ~ 3.5).[21]

The transient absorption spectra produced in the reaction of e_{aq}^- and the 2-hydroxy-2-propyl radical with 2-(arylazo)-1-naphthol-3,6-disulfonate at pH 7.0 are similar to that for the electron adduct[7] of unsubstituted 1-(arylazo)-2-naphthol-6-sulfonate, the transient optical spectrum of which absorbs at 400 and 530 nm. The intensity at higher wavelengths is greater than that at shorter wavelengths, in contrast to the observations for the electron adducts of orange I and methyl orange.

The electron adducts decay bimolecularly with second-order rate constants of $(2.4-5.0) \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 6 and 9 for orange I (Figure 2D), $(2.0-6.0) \times 10^9$ dm^3 mol^{-1} s^{-1} at pH 3 and 7 for methyl orange, and 3×10^9 dm^3 mol^{-1} s^{-1} at pH 7 for 2-(arylazo)-1-naphthol-3,6-disulfonate. The reduction potential of methyl orange ($E(\mathrm{D}/\mathrm{D}^{\bullet-})$) was determined to be −0.66 ± 0.02 V, after correction for ionic strength.

(d) Species Produced by Reaction of $^{\bullet}$OH with the Dyes. The reaction of $^{\bullet}$OH with the various dyes was undertaken to assess whether the $^{\bullet}$OH adducts subsequently eliminate OH^- to form the corresponding one-electron-oxidized species of the dyes. The corrected transient optical absorption spectrum for the species produced in the reaction of $^{\bullet}$OH with orange I at pH 6.6 is shown in Figure 4A. The decrease in the optical absorption with time monitored at 560 nm (Figure 5A) is accompanied by an increase in absorbance monitored at 340 nm (Figure 5B) and 400 nm. The $^{\bullet}$OH adducts of orange I decay bimolecularly (Figure 5D) with a second-order rate constant (2k) of $(0.8-1.3) \times 10^{10}$ dm^3 mol^{-1} s^{-1} determined at 580 nm and pH 6.6. At pH 4.0 the initial species produced in the reaction of $^{\bullet}$OH with orange I is identical with that of the $^{\bullet}$OH adduct observed at pH 6.6.

However, the rate of decrease of optical absorbance at 560 nm increases compared with that at pH 6.6 (data not shown). At pH 10.0, the initial species produced in the reaction of $^{\bullet}$OH with orange I is, however, different from that observed at pH 6.6. It exhibits a broad maximum at 420−500 nm, which decays within 110 μs, leading to a species with an absorption maximum at 340 and 425 nm, as shown in Figure 4B. The spectrum of the resulting species at 110 μs is similar to that of the one-electron-oxidized species of orange I at pH 10.0. The first-order rate of decay of the $^{\bullet}$OH adduct initially produced in the reaction of $^{\bullet}$OH with orange I depends on pH, as shown in Figure 4B (inset a). The initial species produced in the reaction of $^{\bullet}$OH

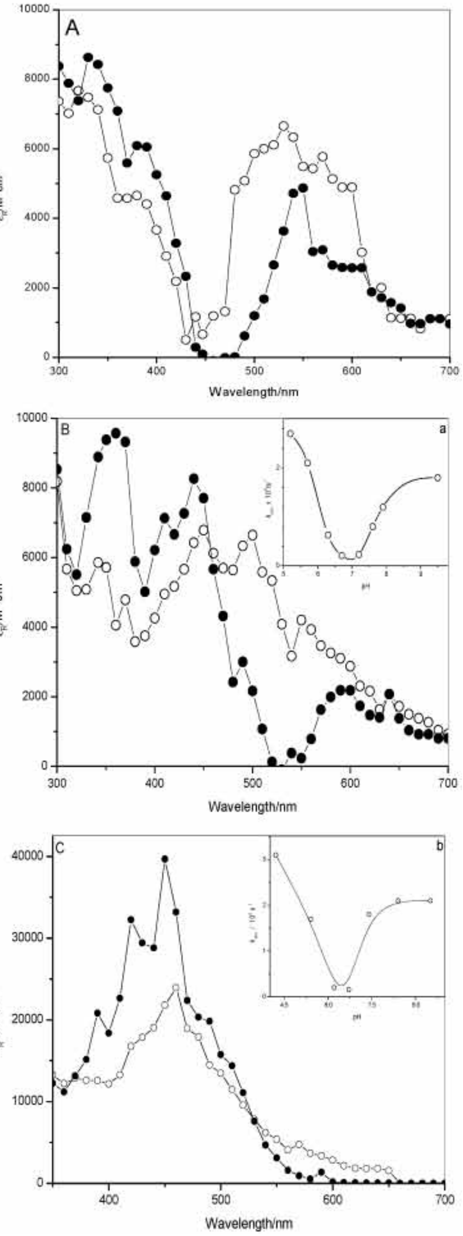


Figure 4. Corrected transient optical absorption spectra formed in the reaction of $^{\bullet}$OH with (A) orange I at pH 6.6 (○, 6 and ●, 120 μs after pulse irradiation) and (B) orange I at pH 10 (○, 6 and, ●, 110 μs after pulse irradiation) and with (C) O-methylated orange I at pH 7.0 (○, 6 and, ●, 250 μs after pulse irradiation). Insets: (a) pH dependence of the first-order rate of decay at 580 nm for the $^{\bullet}$OH adduct of orange I; (b) pH dependence of the first-order rate of decay at 530 nm for the $^{\bullet}$OH adduct of O-methylated orange I. [Dye] = 5 × 10^{-5} mol dm^{-3}. Dose/pulse = 2 Gy.

with orange I is assigned to its $^{\bullet}$OH adduct and it is suggested that it subsequently eliminates water in acid−base-catalyzed reactions to give the one-electron-oxidized species.

The optical absorption spectrum of the initial species produced in the reaction of $^{\bullet}$OH with O-methylated orange I is shown in Figure 4C. This species then undergoes a first-order decay, the rate of which depends on pH, as shown in Figure 4C (inset b). The initial species produced in the reaction of $^{\bullet}$OH with O-methylated orange I is assigned to its $^{\bullet}$OH adduct, which eliminates OH^{-} in acid−base-catalyzed reactions to give the one-electron-oxidized species.

Consistent with previous observations with the $^{\bullet}$OH adducts of 1-(arylazo)-2-naphthol-6-sulfonate,[7] the $^{\bullet}$OH adduct of 2-(arylazo)-1-naphthol-3,6-disulfonate, the optical absorption spectrum of which is similar to that with 1-(arylazo)-2-naphthol-6-sulfonate (data not shown), is stable to OH^{-} elimination. That water elimination occurs from orange I and O-methylated orange I reflects their similarity to phenols, i.e., electron-donating effect of the hydroxy and methoxy groups and absence of the electron-withdrawing sulfonate group. Further, with 1-(arylazo)-2-naphthol and 2-(arylazo)-1-naphthol, their pK_a and redox potentials are very different from those for phenols or orange I, partly because the hydroxyl group may hydrogen bond with the azo group. The $^{\bullet}$OH adduct of 2-(arylazo)-1-naphthol-3,6-disulfonate decays bimolecularly with a rate constant (2k) of 1.4 × 10^{10} dm^{3} mol^{-1} s^{-1}, determined at 560 nm and a pH of 7.0.

(e) Stoichiometry of Radical-Induced Decolorization of the Dyes. The stoichiometry for 2-hydroxy-2-propyl radical-induced loss of orange I, determined from the pulse radiolysis data in Figure 2C, indicates that 1 dye molecule is removed per 1.8 2-hydroxy-2-propyl radicals. Using a low dose rate 10 Gy/min of γ-irradiation at pH 6.6, the stoichiometry for 2-hydroxy-2-propyl radical-induced loss of orange I is one dye molecule per 2.2 2-hydroxy-2-propyl radicals (data not shown). This stoichiometry is consistent with the loss of the one-electron-reduced radicals of orange I to form products involving radical−radical disproportionation.

The interaction of $^{\bullet}$OH with the dyes leads to loss of absorbance in the visible absorption band of the ground state of the dyes. From pulse radiolysis data at 480 nm with orange I, 9.9 × 10^{-7} mol dm^{-3} of $^{\bullet}$OH results in a loss of 9.8 × 10^{-7} mol dm^{-3} of the dye at pH 6.6, corresponding to a stoichiometry of 1 dye molecule per 1 $^{\bullet}$OH (Figure 5C), whereas at pH 10.0, when the $^{\bullet}$OH adduct of orange I is rapidly converted through water elimination into the one-electron-oxidized radical, 1 dye molecule is lost per 2.2 $^{\bullet}$OH. Using a low dose rate 10 Gy/min of γ-irradiation at pH 6.6, the stoichiometry for $^{\bullet}$OH-induced loss of orange I is one dye molecule per 2 $^{\bullet}$OH. Therefore, these differences in the stoichiometry under high [radical] (pulse radiolysis) and low [radical] (γ-radiolysis) conditions at pH 6.6 can be explained on the basis of a competing bimolecular decomposition of the $^{\bullet}$OH adducts of orange I by radical−radical dimerization with a first-order elimination of OH^{-} to give one-electron-oxidized radicals of orange I, which decay bimolecularly by radical−radical disproportionation. The stoichiometry at pH 7.0 determined from pulse radiolysis data for loss of the $^{\bullet}$OH adduct of 2-(arylazo)-1-naphthol-3,6-disulfonate is 1 dye molecule per 1 $^{\bullet}$OH, consistent with that when the $^{\bullet}$OH adducts of orange I decay bimolecularly and with previous data with 1-(arylazo)-2-naphthol-6-sulfonate.[7]

(f) Reaction Mechanisms. Our earlier study[7] on 1-(arylazo)-2-naphthol-6-sulfonate dyes with $N_3^{\bullet}$ had clearly shown that $N_3^{\bullet}$ reacts via an outer sphere electron-transfer process, leading to the formation of the one-electron-oxidized species of the dyes. A similar mechanism is proposed for the oxidation of orange I and 2-(arylazo)-1-naphthol-3,6-disulfonate by $N_3^{\bullet}$. The initial reaction involves electron transfer to give radical cation/naphthoxyl radical **1** in Schemes 2 and 3. With orange I, the radical species **1** (see Scheme 2) has a pK_a value of 4.6. From the stoichiometry for the loss of orange I, the one-electron-oxidized radicals decay bimolecularly by radical−radical disproportionation. $N_3^{\bullet}$ oxidizes methyl orange to give its one-electron-oxidized radical, **2** in Scheme 1S. As discussed earlier, this oxidation preferentially occurs at the anilino ring, a reflection of the higher reactivity of methyl orange than that of O-methylated orange I with $N_3^{\bullet}$.

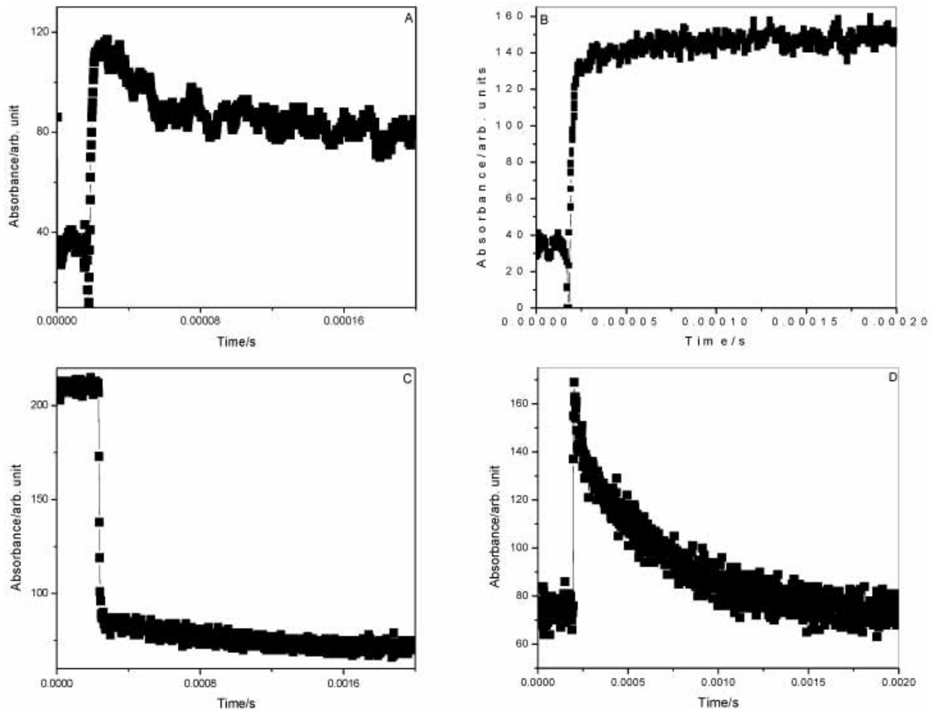
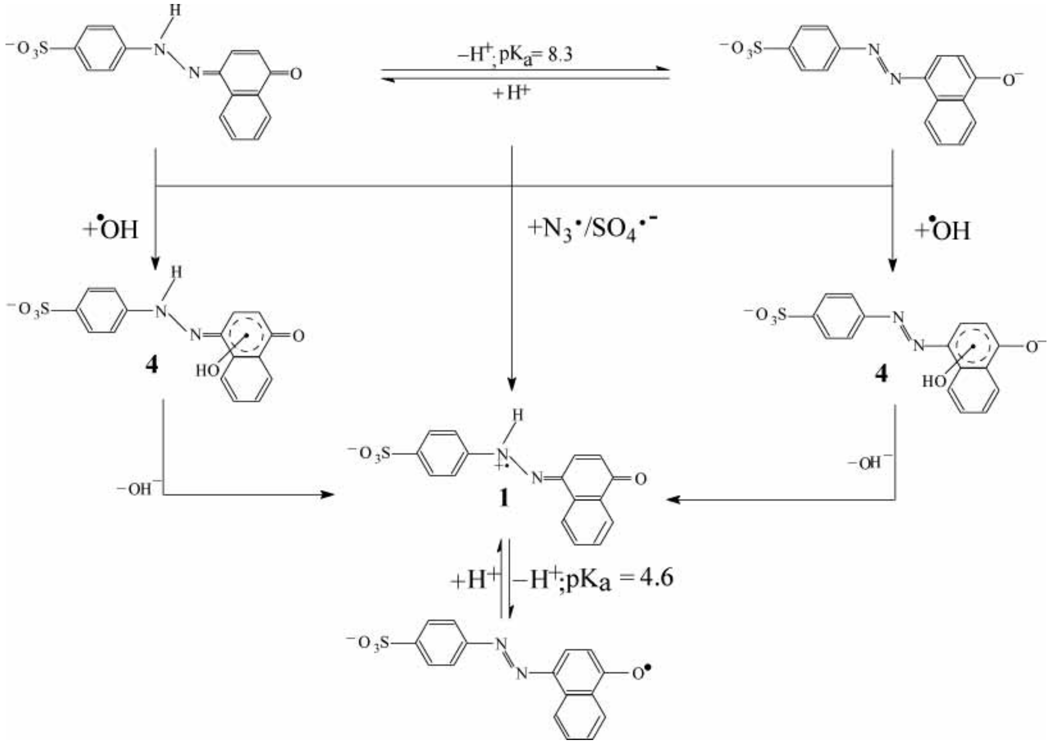


Figure 5. Traces showing (A) decay of the $^{\bullet}$OH adduct of orange I at 560 nm, (B) absorption buildup at 340 nm for the reaction of $^{\bullet}$OH with orange I, (C) optical absorbance changes with time for reaction of $^{\bullet}$OH with orange I at 480 nm at pH 6.6, and (D) decay at 560 nm for the reaction of $^{\bullet}$OH with orange I at pH 6.6. [Dye] = 5×10^{-5} mol dm^{-3}. Dose/pulse = 2 Gy.

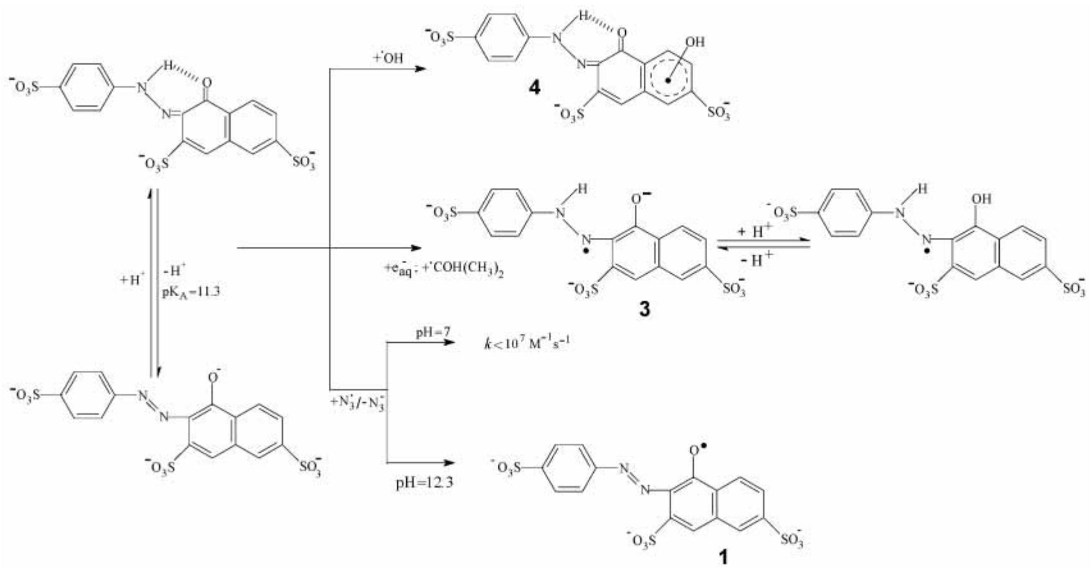
SCHEME 2: Oxidation of Orange I by $^{\bullet}$OH and $N_3^{\bullet}$



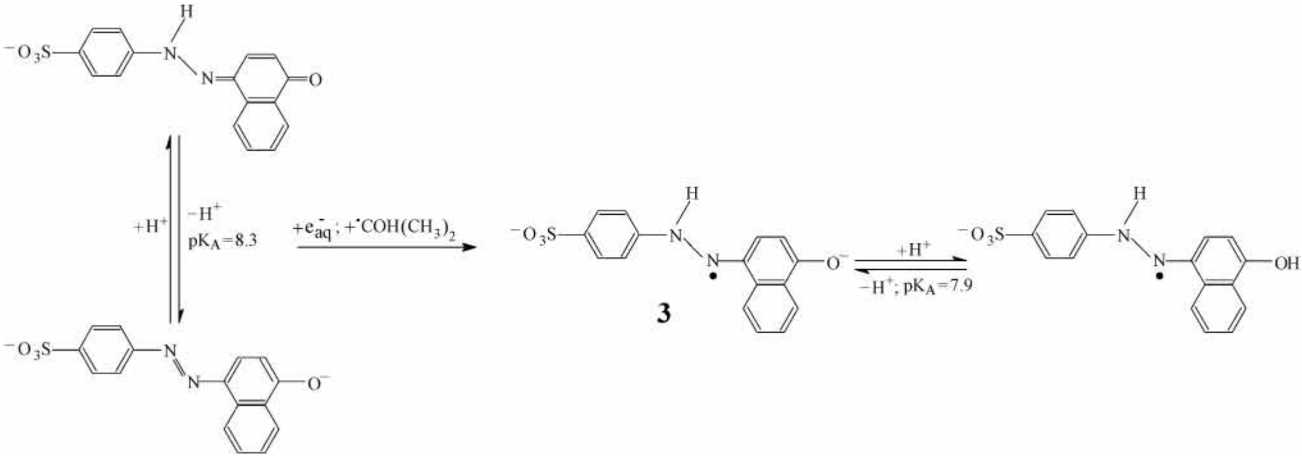
It is proposed that one-electron reduction of orange I, methyl orange and 2-(arylazo)-1-naphthol-3,6-disulfonate by 2-hydroxy-2-propyl radical/e_{aq}^{-} at pH 7 involves nucleophilic attack to form the one-electron-reduced adducts. These adducts on protonation give their corresponding hydrazyl radicals (**3** in Schemes 3 and 4 and 1S). With orange I, the one-electron-reduced species has a pK_a of 7.9, due to protonation of the hydroxyl group, as shown in Scheme 4. The one-electron-reduced adducts decay bimolecularly, and from the stoichiometry for loss of orange I at pH 6−7, it is inferred that the radicals mainly decay bimolecularly by radical−radical disproportionation to give products, the stability of which are not known at pH 5−10.

Similar to the mechanism proposed for $^{\bullet}$OH addition to the 1-(arylazo)-2-naphthol-6-sulfonate dyes,[7] it is suggested that the reaction of the $^{\bullet}$OH with orange I, O-methylated orange I, and 2-(arylazo)-1-naphthol-3,6-disulfonate involves $^{\bullet}$OH addition mainly to the naphthol-ring system to give adducts **4** shown in

SCHEME 3: Oxidation ($^•$OH and $N_3^•$) and Reduction (e_{aq}^- and the 2-Hydroxy-2-propyl Radical) of 2-(Arylazo)-1-naphthol-3,6-disulfonate



SCHEME 4: Reduction of Orange I by e_{aq}^- and the 2-Hydroxy-2-propyl Radical



Schemes 2, 3, and 2S, although a lesser contribution of adducts may arise by addition of $^•$OH to the phenyl ring. In contrast to the $^•$OH adducts of 2-(arylazo)-1-naphthol-3,6-disulfonate, which are stable to OH$^-$ elimination, the $^•$OH adducts of orange I and O-methylated orange I subsequently eliminate H_2O in an acid−base-catalyzed reaction to give their corresponding one-electron-oxidized radicals, as shown in Schemes 2 (radical **1**) and 2S (radical **3**). The resulting one-electron-oxidized radical of orange I undergoes bimolecular decomposition predominantly by radical−radical disproportionation.

Conclusions

The ease of oxidation and reduction of the dyes but not their reactivity with $^•$OH depends on their tautomeric form. With orange I, one-electron oxidation is most efficient with its common anion whereas one-electron reduction is more efficient with the azonium and hydrazone forms. In both cases, the resulting radical intermediates mainly decay biomolecularly by radical−radical disproportionation The $^•$OH is efficient at removing the dyes by bimolecular processes involving radical−radical dimerization and its reactivity is independent of the tautomeric forms of the dyes studied. For orange I and its O-methylated derivative, the $^•$OH adducts are also unstable with respect to OH$^-$ elimination; i.e., they behave like simple phenols. In such cases, the efficiency of removal of the dye by the $^•$OH is critically dependent on the pH and the competition between the bimolecular decay of the $^•$OH adducts and the first-order water elimination pathway.

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Supporting Information Available: Figure 1S shows the optical absorption spectra of the one-electron-oxidized radical of 2-(arylazo)-1-naphthol dye. Scheme 1S shows the oxidation and reduction of methyl orange. Scheme 2S shows the mechanism of oxidation of O-methylated orange I by $^•$OH. This material is available free of charge via the World Wide Web at http://pubs.acs.org.

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