Free-Radical-Induced Oxidation and Reduction of 1-Arylazo-2-naphthol Dyes: A Radiation Chemical Study

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Received: November 1, 2001; In Final Form: January 14, 2002

The kinetics and transient optical absorption spectra of the intermediates formed in the reaction of $^{\bullet}$OH, $N_3^{\bullet}$, and e^-_{aq} with 1-arylazo-2-naphthol and its ortho- and para-substituted chloro, methyl and methoxy derivatives at pH 7.0 have been studied by pulse radiolysis. The rate constants for the reaction of $^{\bullet}$OH and the nucleophilic hydrated electron (e^-_{aq}) with these compounds are $(1.0-1.2) \times 10^{10}$ M^{-1} s^{-1} and $(0.8-2.5) \times 10^{10}$ M^{-1} s^{-1}. The reaction of $N_3^{\bullet}$ with these azo dyes is more selective ($\rho^+ = -2.0$) with the rate constants varying between 0.1×10^9 and 8×10^9 M^{-1} s^{-1} depending upon the substituent. The transient optical absorption spectra of the intermediates formed in the reaction of the dyes with $^{\bullet}$OH are different from the corresponding spectra of the intermediates observed in the reaction of the dyes with $N_3^{\bullet}$. The $^{\bullet}$OH radical reacts with the dyes by addition to form the $^{\bullet}$OH adducts, whereas $N_3^{\bullet}$ reacts with the dyes by direct one-electron transfer to form the one-electron oxidized dye radical. The pK_A of the dye radical of the para-methoxy derivative was determined to be 5.2. This radical decays bimolecularly, predominantly by disproportionation, whereas the $^{\bullet}$OH adducts of the dyes also decay bimolecularly but predominantly by dimerization. The initially formed radical anion in the reaction of e^-_{aq} with the unsubstituted dye protonates rapidly to give the hydrazyl radical, which decays bimolecularly by disproportionation. Of the radicals studied, the $^{\bullet}$OH-induced oxidation of the dyes is the most effective process leading to decolorization of the dyes at pH 7.0.

Introduction

Azo dyes find a wide range of applications in the textile, paper, food, cosmetics, agrochemical, and pharmaceutical industries. They are characterized by the presence of the chromophoric azo group (−N═N−) attached to the substituents, mainly benzene or naphthalene derivatives containing electron-withdrawing or -donating groups or both. Because of their high solubility in water, they are transported over long distances when discharged into water.

Because most of the dyes are designed to resist chemical and photochemical degradation processes, it is difficult to remove them completely from industrial effluent. Several methods including advanced oxidation processes have been developed for this purpose. The degradation of these dyes to eliminate color and partial mineralization is achieved by photolysis in the presence of H_2O_2,[1−4] photocatalytic and TiO_2 catalyst,[5−8] Fenton's reaction,[9,10] sonolysis,[11−13] enzyme-catalyzed oxidation,[14] and radiolysis by gamma[15] and high-energy electron beams.[16,17] Oxidation by singlet oxygen also contributes to the photodegradation of arylazo naphthol[18] dyes. However, for dyed fabrics, it is necessary that the dyes should remain fast to potential oxidation during normal washing processes[19,20] and through interactions with the base fabric.[21,22] Azo compounds are reduced[23] by the intestinal anaerobic bacteria through scission of azo bonds to form aromatic amines, which are toxic to living organisms. Therefore, the fate of the byproducts formed and their effect on living organisms have made it necessary to understand the underlying reaction mechanisms and product distribution following the oxidation/reduction of these dyes.

The rates of reaction of azobenzene, the simplest azo dye, with the hydrated electron (e^-_{aq}), alcohol radicals,[24,25] and hydroxyl radicals[26] ($^{\bullet}$OH) are diffusion controlled. α-Hydroxyalkyl radicals and e^-_{aq} form hydrazyl radicals,[27] and the $^{\bullet}$OH radicals interact to give $^{\bullet}$OH adducts.[26] The reaction of $^{\bullet}$OH with an amino-substituted azobenzene (acid yellow 9) involves[28] both $^{\bullet}$OH adduct formation and electron transfer, whereas the sulfate radical anion ($SO_4^{\bullet -}$) reacts exclusively by electron transfer. The one-electron oxidized and reduced forms of 2-hydroxynaphthalene azobenzene sulfonate (acid orange 7) and of substituted diazobenzene dyes have been characterized[6,8] by their optical absorption spectra. The reaction of $^{\bullet}$OH with methyl orange and calmagite produces[29] the anilino radical cation and hydroxycyclohexadienyl radicals. Plausible mechanistic pathways proposed involve free radical oxidation/reduction of these azo dyes to give products that are transparent in the visible region.

In this study, 1-arylazo-2-hydroxynaphthalene-6-sodium sulfonate (unsubstituted azo dye) and its ortho- and para-methoxy, -chloro, and -methyl derivatives (Scheme 1) have been chosen as target molecules for investigation of their oxidation and

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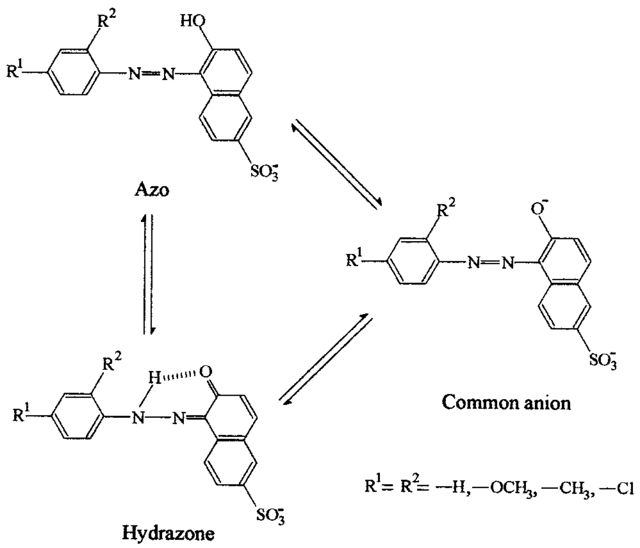
10.1021/jp014025b CCC: $22.00

SCHEME 1: Structural Forms of 1-Arylazo-2-naphthol Dyes



reduction initiated by radicals generated pulse radiolytically. An understanding of these processes may give insight into the reaction pathways leading to decolorization of the dyes. These dyes predominantly exist in neutral aqueous solutions in the hydrazone tautomeric form,[30a] which is responsible for the dark colors. Although the hydrazone tautomer is the reactive form toward the perhydroxyl anion,[30a,31] the dye common anion is the reactive species during the oxidation by peracids and hypochlorites. Because the pK_A values of the ground-state dyes are >10, at pH 7.0 the dyes are most likely to react with the $^{\bullet}$OH in their hydrazone form. In addition, these dyes do not aggregate at low concentrations to produce complicated kinetic data.[30a] Kinetic investigation of the reactions of these dyes with oxidants such as hypochlorite, peracids, and hydrogen peroxide in aqueous media in the presence or absence of trace metals has already been reported by Oakes and co-workers.[30] The reaction of $N_3^{\bullet}$ with these dyes at pH 12, at which the dye exists mainly in its common anion form, indicated the formation of the one-electron oxidized dye radical.[32] This study was undertaken to characterize the species formed on reaction of $^{\bullet}$OH, $N_3^{\bullet}$, and the solvated electrons (e^-_{aq}) with these azo dyes at pH 7.0 at which the dyes are present mainly in their hydrazone tautomeric form.

Experimental Section

Preparation of Solutions. The synthesis, purification, characterization, and properties of the unsubstituted azo dye and its ortho- and para-methoxy, -chloro, and -methyl derivatives have been described elsewhere.[30c,f] Their purity was checked by HPLC and found to be ≥95% pure with the exception of the ortho-chloro derivatives, where its purity is ≥80%. Further purification was difficult, because the impurities are mainly salt and water, but they are not expected to influence the pulse-radiolysis experiments. All other chemicals were of reagent grade and were used as supplied. Solutions were freshly prepared by using water purified by a Millipore Milli-Q system. All experiments were carried out at room temperature. The pH of the solutions was determined by using a Mettler Delta 340 pH meter, and the ground-state absorption of the dyes was measured just before irradiation using a Beckman DU 7400 spectrophotometer equipped with a diode array detector.

Irradiations. Radiolysis of aqueous solutions with high-energy electrons and γ-rays leads to the generation of primary radiolytic products the yields of which are known (reaction 1).

$$H_2O \rightsquigarrow {}^{\bullet}OH,\ H^{\bullet},\ e^-_{aq},\ H_2O_2,\ H_2,\ H_3O^+$$

$$G_{e^-_{aq}} = G_{OH} = 0.28\ \mu M\ J^{-1}, \quad G_H = 0.055\ \mu M\ J^{-1} \qquad (1)$$

The e^-_{aq} may be quantitatively converted into $^{\bullet}$OH by saturating the aqueous solution with N_2O (reaction 2).

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + {}^{\bullet}OH + OH^-$$

$$k = 8.7 \times 10^9\ M^{-1}\ s^{-1} \quad \text{at} \quad \text{pH } 7^{33} \qquad (2)$$

$N_3^{\bullet}$ was generated in N_2O-saturated, aqueous solution containing 20 mM NaN_3, where the $^{\bullet}$OH is converted into $N_3^{\bullet}$ (reaction 3).

$${}^{\bullet}OH + N_3^- \rightarrow N_3^{\bullet} + OH^-$$

$$k = 1.2 \times 10^{10}\ M^{-1}\ s^{-1} \quad \text{at} \quad \text{pH } 7^{33} \qquad (3)$$

To investigate the reaction of e^-_{aq}, the solutions were deaerated and contained 2-methylpropan-2-ol (0.2 M) as a scavenger of $^{\bullet}$OH (reaction 4).

$${}^{\bullet}OH + (CH_3)_3COH \xrightarrow{N_2} {}^{\bullet}CH_2C(CH_3)_2OH + H_2O$$

$$k = 7.6 \times 10^8\ M^{-1}\ s^{-1} \quad \text{at} \quad \text{pH } 7^{33} \qquad (4)$$

$SO_4^{\bullet-}$ was generated in deaerated, aqueous solutions containing 15 mM $Na_2S_2O_8$ and 20 mM 2-methylpropan-2-ol as a scavenger of $^{\bullet}$OH (reaction 5).

$$S_2O_8^{2-} + e^-_{aq}({}^{\bullet}H) \rightarrow SO_4^{\bullet-} + SO_4^{2-}(HSO_4^-)$$

$$k_{e^-_{aq}} = 1.2 \times 10^{10}\ M^{-1}\ s^{-1} \quad \text{at} \quad \text{pH } 7^{33}$$

$$k_{H^{\bullet}} = 2.5 \times 10^7\ M^{-1}\ s^{-1} \quad \text{at} \quad \text{pH } 7^{33} \qquad (5)$$

High-energy electron pulses (7 MeV, 50 ns and 4.3 MeV, 1.6 μs) were used for pulse radiolysis experiments, and details of the two linear accelerator facilities used have been described elsewhere.[34a−c] Dosimetry was carried out before each experiment with aerated, aqueous solutions containing 10 mM KSCN and taking $G\epsilon_{500nm} = 2.6 \times 10^{-4}\ m^2\ J^{-1}$ for the transient[35a,b] $(SCN)_2^{\bullet-}$. The known dose per pulse used was in the range 3−10 Gy, producing a maximum [radical] of ≤6 μM.

The accuracy of the rate constants determined for reaction of $^{\bullet}$OH, $N_3^{\bullet}$, and e^-_{aq} with these dyes is within ±10%, except for the para-chloro derivative for which it is ±20%.

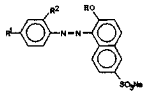
***γ*-Irradiation.** γ-Irradiation was carried out using a well-type Co^{60} γ-source in the Department of Chemistry, University of Pune. The dose rate, which was determined using Fricke dosimetry, was 11 Gy min^{-1}.

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 6 to determine the extinction coefficients of

$$\epsilon_{radical} = \epsilon_{parent} + \frac{OD_{measured}(G\epsilon^{\lambda})_{dosimeter}}{G_{radical}\ (OD^{\lambda})_{dosimeter}} \qquad (6)$$

the radicals ($\epsilon_{radical}$). Equation 6 accounts for bleaching of the reacted parent compound after passage of the electron pulse. Equation 6 uses the molar absorptivity of the parent compound

TABLE 1: Second-Order Rate Constants ($k/10^{10}$ M^{-1} s^{-1}) for the Reaction of $^{\bullet}OH$, $N_3^{\bullet}$, and e^-_{aq} with 1-Arylazo-2-naphthol Dyes at pH 7.0

Compound  (pK_a)	$^{\bullet}OH$	$N_3^{\bullet}$	e_{aq}^-
	k	*k*	*k*
Unsubstituted dye $R^1 = R^2 = H$, (10.8)	1.1	0.07	2.5
o- methoxy dye $R^1 = H$, $R^2 = OCH_3$, (11.4)	1.0	0.4	1.5
p- methoxy dye $R^1 = OCH_3$, $R^2 = H$, (10.8)	1.1	0.8	0.8
p- chloro dye $R^1 = Cl$, $R^2 = H$, (10.5)	1.0	0.05	1.9
p- methyl dye $R^1 = CH_3$, $R^2 = H$, (10.9)	1.2	0.2	1.6

(ϵ_{parent}) and the absorbed dose to calculate $\epsilon_{radical}$ using the optical absorbance determined at the wavelength investigated ($OD_{measured}$).

Results and Discussion

(a) Evaluation of Kinetics. *(i) Reaction of $^{\bullet}OH$ with the Dyes.* The rate constants for reaction of $^{\bullet}OH$ with the unsubstituted azo dye and its ortho- and para-methoxy, -chloro, and -methyl derivatives were determined in N_2O-saturated, aqueous solution at pH 7.0. From the linear dependence of the first-order rate of growth of the transient optical absorption in the wavelength region 350−370 nm on the concentration of the azo dyes ($(0.2-1) \times 10^{-4}$ M), the second-order rate constants were evaluated and are given in Table 1. The rate constants are independent of the substituents. The rate constants for the reaction of $^{\bullet}OH$ with the unsubstituted dye were also determined at pH 4.3 and 10.3 and are the same as those determined at pH 7.0. These values are in agreement with those reported[26,28,29] for other azo dyes, azobenzene, acid yellow 9, methyl orange, and calmagite.

(ii) Reaction of $N_3^{\bullet}$ with the Dyes. The rate constants for reaction of $N_3^{\bullet}$ with the unsubstituted azo dye and its derivatives ($(0.2-1) \times 10^{-4}$ M) were determined from the linear dependence of the first-order rate of formation of the transient species of the dyes on the dye concentration at pH 7.0 and are tabulated in Table 1. The rate of formation of the optical absorption at 360−370 nm and 560−600 nm are the same as that for the loss of the ground-state optical absorption at 490 nm. The bimolecular rate constants for the reaction of $N_3^{\bullet}$ with the azo dyes are lower than those for the reaction with $^{\bullet}OH$ and depend significantly on the substituents. The lowest rate constant was determined with the para-chloro derivative, whereas the highest value was determined with the para-methoxy-substituted dye. The order for the second-order rate constants decreases among the substituted dyes: para-methoxy > ortho-methoxy > para-methyl > unsubstituted > para-chloro. Even at the highest concentration of 0.1 mM, reaction of $N_3^{\bullet}$ with the ortho-chloro derivative was not observed, indicating that its rate constant with $N_3^{\bullet}$ is $<1 \times 10^8$ M^{-1} s^{-1}. The second-order rate constant for the reaction of $N_3^{\bullet}$ with the unsubstituted dye determined at pH 12.0 is 5.2×10^9 M^{-1} s^{-1}, which is higher by an order of magnitude than that at pH 7.0. To quantify the effects of substituents, the data were analyzed on the basis of the Hammett equation. The dependence of the rate constant for oxidation of the dyes by $N_3^{\bullet}$ on σ_p^+ values for the para-substituted derivatives is shown in Figure 1. The ρ^+ value calculated from the slope of this dependence is -2.0 ± 0.1.

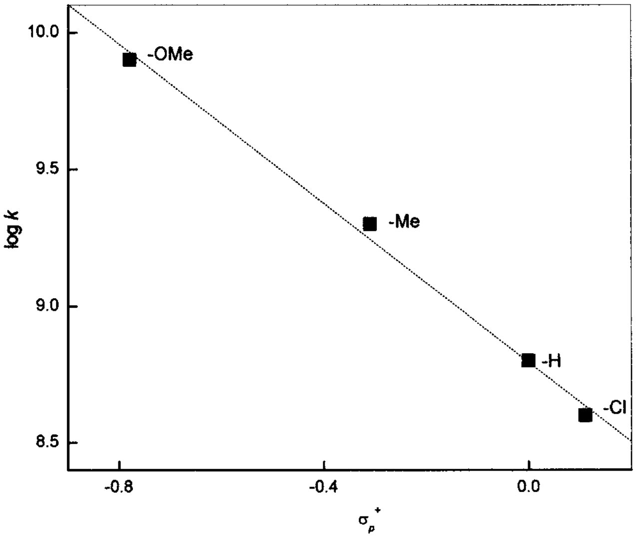


Figure 1. Hammet plot of the dependence of the rate constants for reaction of $N_3^{\bullet}$ with para-substituted azo dyes on the value of σ_p^+.

The reactions of $N_3^{\bullet}$ and $SO_4^{\bullet -}$ with the dyes are generally more selective than the corresponding reaction with $^{\bullet}OH$. This is evident from the ρ^+ values found for the reaction of $^{\bullet}OH$ with substituted benzenes ($\rho^+ = -0.5$), pyrimidines ($\rho^+ = -0.7$) and purines ($\rho^+ \approx -1.0$), reported by others[36−39] as well as by our group.[41−43] In contrast, a relatively high value of ρ^+ of -1.5 was reported[40] for the reaction of $SO_4^{\bullet -}$ with substituted benzenes. From the ρ^+ value of -2.0 determined in this study for the reaction of $N_3^{\bullet}$ with the unsubstituted dye and its derivatives, it is suggested that the reaction of $N_3^{\bullet}$ with the dyes proceeds predominantly via an outer-sphere electron-transfer mechanism. Further, the higher second-order rate constant at pH 12.0 shows that the common anion form of the dyes is more easily oxidized than the hydrazone tautomer.

(iii) Reaction of e^-_{aq} with the Dyes. The rate constants for reaction of the nucleophilic e^-_{aq} with the unsubstituted azo dye and substituted derivatives at pH 7.0 were determined from the decay of e^-_{aq} monitored at 700 nm. The second-order rate constants determined for the reaction of e^-_{aq} with these azo dyes are close to diffusion-controlled and are shown in Table 1. The decay of the optical absorbance of e^-_{aq} coincided with an increase in optical absorption at 350 and 550 nm. The rate constants for reaction of e^-_{aq} with the substituted dyes are similar, the highest *k* value corresponding to the unsubstituted dye and the lowest to the para-methoxy derivative. The rate constant measured with the unsubstituted dye is comparable with that reported[24,25] for reaction of azobenzene and 4-nitroazobenzene with e^-_{aq} ($k \approx (1-2) \times 10^{10}$ M^{-1} s^{-1}), but is larger by an order of magnitude for reduction of the diazo dye[8] (naphthol blue black). The rate constants for reaction of e^-_{aq} with substituted arylazo naphthol dyes observed in this study are higher than those reported[33] with the corresponding substituted benzenes containing $-OCH_3$, $-CH_3$, or $-Cl$ groups.

(b) Transient Absorption Spectra. *(i) Reactions of $^{\bullet}OH$ and $N_3^{\bullet}$.* The corrected transient optical absorption spectrum for the species produced in the reaction of $^{\bullet}OH$ with the unsubstituted azo dye, determined 7 μs after pulse irradiation, shown in Figure 2A, exhibits a broad maximum in the range 425−550 nm. The transient optical absorption spectra of the species

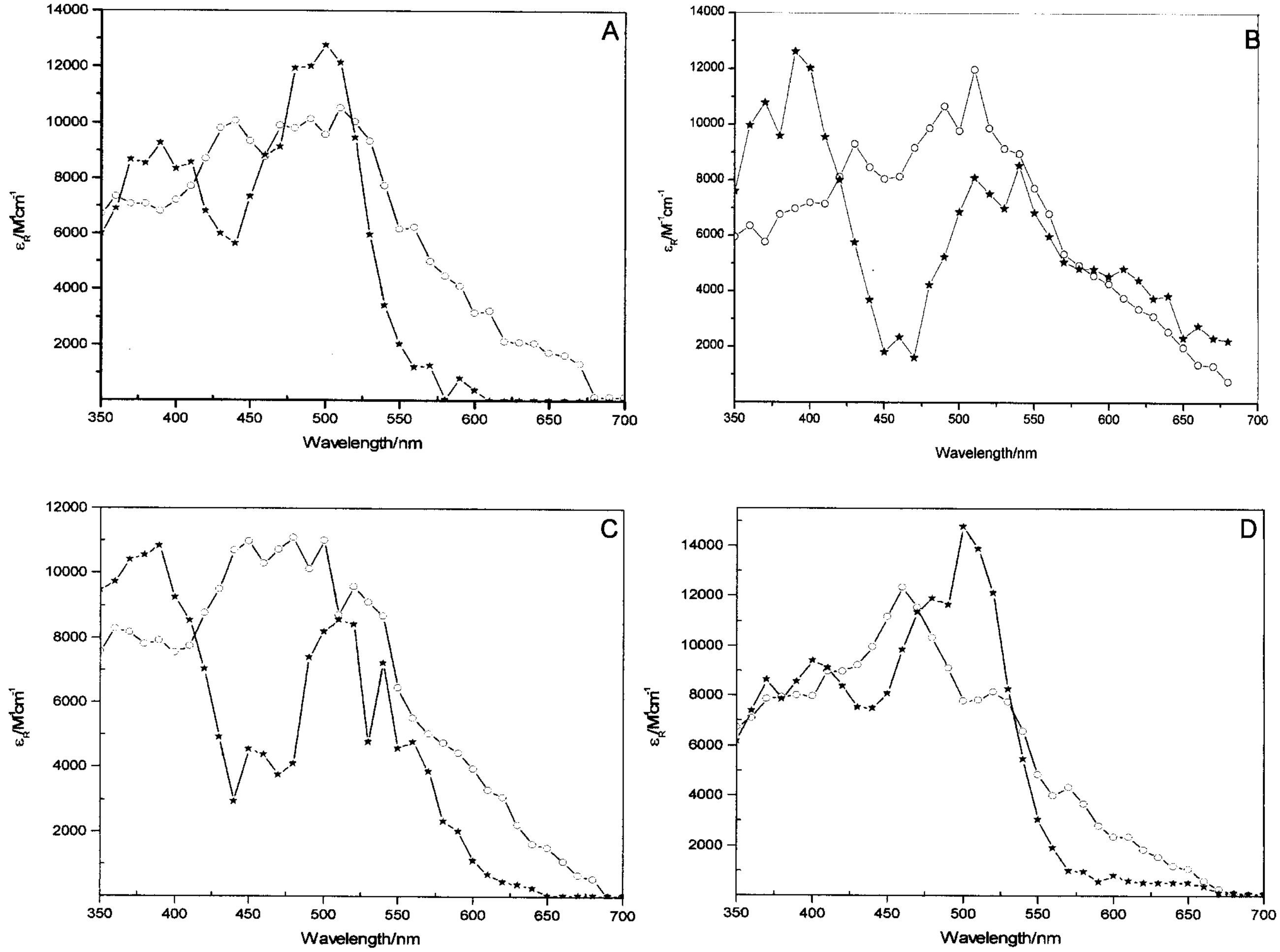


Figure 2. Corrected transient optical absorption spectra of the species formed in the reaction of $^{\bullet}$OH (○, 7 μs after the radiation pulse) and $N_3^{\bullet}$ (★, 30 μs after the radiation pulse) with (A) unsubstituted dye, (B) ortho-methoxy-substituted dye, (C) para-methyl-substituted dye and (D) para-chloro-substituted dye at pH 7.0. [Dye] = 50 μM; dose/pulse = 4 Gy.

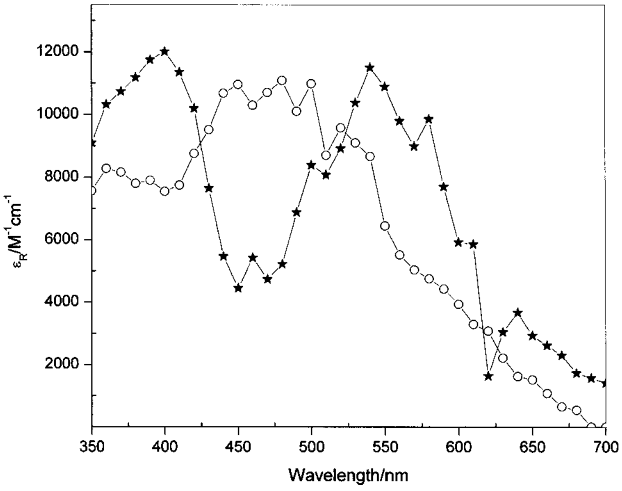


Figure 3. Corrected transient optical absorption spectra obtained in the reaction of $^{\bullet}$OH (○, 7 μs after pulse irradiation) and $N_3^{\bullet}$ (★, 20 μs after pulse irradiation) with 50 μM para-methoxy-substituted dye at pH 7.0. Dose/pulse = 4 Gy.

produced on reaction of $^{\bullet}$OH with the unsubstituted dye determined at pH 4.3 and 10.3 is identical to that determined at pH 7.0. The corrected transient optical absorption spectra for the species produced on reaction of $^{\bullet}$OH with the other derivatives are shown in Figures 2B−D and 3. As can be seen, the spectral characteristics of the species formed in the reaction of $^{\bullet}$OH with para-methoxy, -chloro, and -methyl and ortho-methoxy derivatives are more or less similar to that observed with the unsubstituted dye. These species are assigned to the $^{\bullet}$OH adducts of the respective dyes.

The kinetics of decay of the $^{\bullet}$OH adducts of these azo dyes at pH 7.0 were determined to be bimolecular from the dependence of the change of optical absorbance at 560 nm with time. The bimolecular decay of the transient species was also confirmed from the inverse proportionality of the first half-life of the dye radicals on their concentration, which is directly related to the dose/pulse used (3−10 Gy). The second-order rate constants for the decomposition reaction of the $^{\bullet}$OH adducts of all of the dyes studied were determined to be $(0.9-1.3) \times 10^{10}$ M^{-1} s^{-1}.

The bimolecular decay of the $^{\bullet}$OH adducts of the unsubstituted dye results in loss of optical absorption at wavelengths within the visible absorption band of the ground state of the dye, as shown in Figure 4. Following the initial loss of absorption at 490 nm (Figure 4A), due to the interaction of the dye with $^{\bullet}$-OH, the subsequent loss of absorbance occurs on the same time scale as the loss of the $^{\bullet}$OH adducts determined at 560 nm (Figure 4B). The changes of absorbance with time in Figure 4 are consistent with dimerization of the $^{\bullet}$OH adducts to give product(s) that absorb less than the parent (see below). The other derivatives also show similar decay characteristics to that of the unsubstituted dye.

The radiation chemical yield for $^{\bullet}$OH-induced loss of the unsubstituted dye was determined following γ-irradiation of a

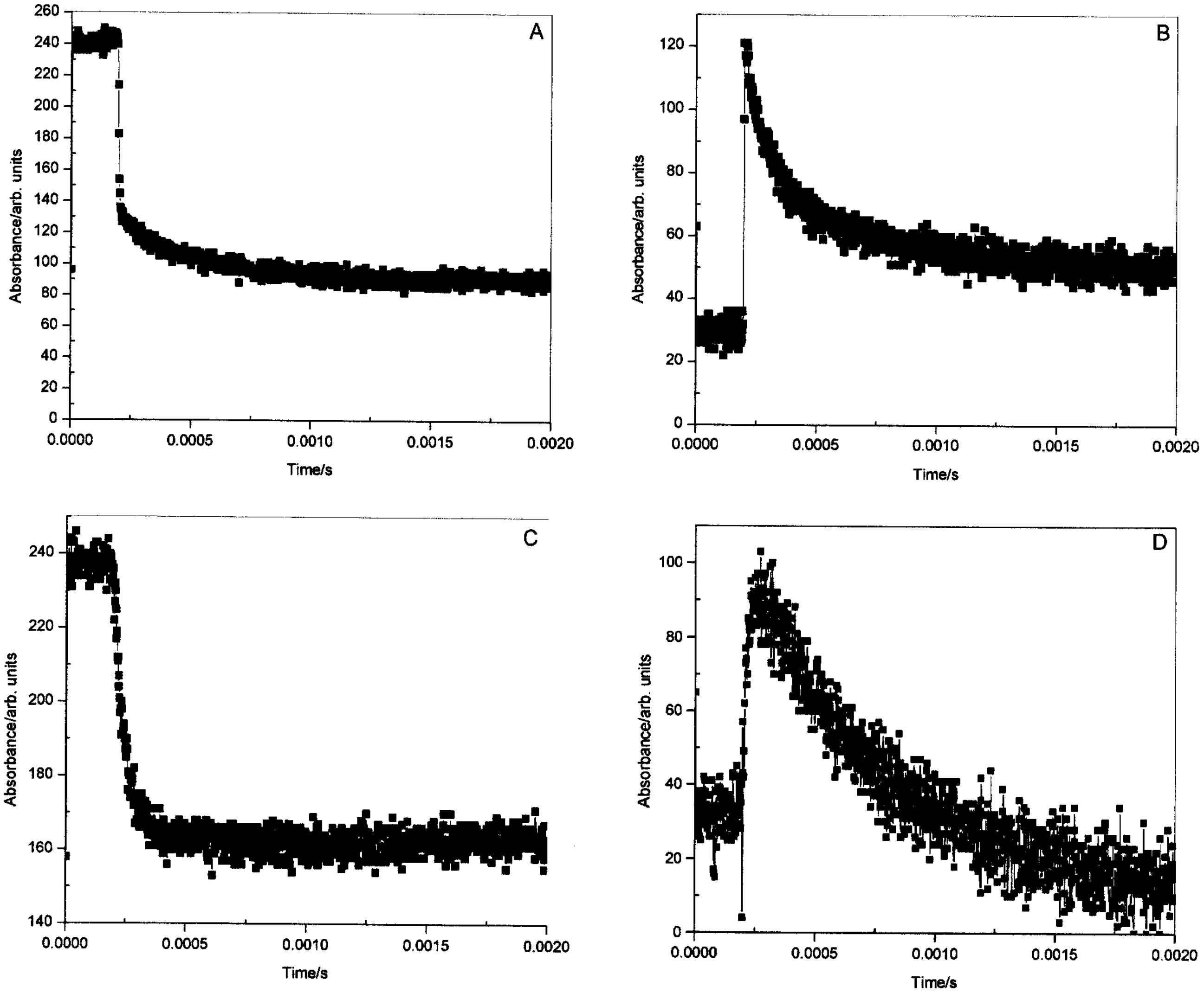


Figure 4. Optical absorbance changes with time for reaction of $^{\bullet}$OH (A,B) and $N_3^{\bullet}$ (C,D) with the unsubstituted dye determined at 490 (A,C), 560 (B), and 540 nm (D) for pulse irradiation of an aqueous solution containing 50 μM unsubstituted dye at pH 7.0. Dose/pulse = 4 Gy.

N_2O-saturated, aqueous solution containing 0.1 mM dye. The dependence of the optical absorption of the solution on radiation dose was determined from the spectrophotometric changes at 490 nm, the maximum optical absorption of the dye. The dependence of the decrease in optical absorbance on radiation dose is linear as shown in Figure 5. From the slope of this dependence, the loss of dye was determined to be (5.2 ± 0.3) $\times 10^{-7}$ M Gy^{-1} assuming that product(s) formed do not absorb at 490 nm. This yield corresponds to the yield of $^{\bullet}$OH of 5.5 $\times 10^{-7}$ M Gy^{-1}. Therefore, one molecule of dye is removed per $^{\bullet}$OH, in agreement with the bimolecular reaction of the $^{\bullet}$OH adducts of the dye occurring by dimerization. From pulse radiolysis data at 490 nm (see Figure 4A), it is calculated that 1.9 μM of the unsubstituted dye was consumed by 2.2 μM of $^{\bullet}$OH, determined from the dose/pulse delivered (4 Gy). This stoichiometry of approximately one unsubstituted dye molecule being removed per $^{\bullet}$OH is consistent with the dimerization of the $^{\bullet}$OH adducts, although a reaction involving H atom transfer between the radicals would also be consistent with the stoichiometry determined.

In the presence of O_2 ([O_2] ≈ 15−25 μM), the transient species produced in the reaction of $^{\bullet}$OH with the unsubstituted dye does not appear to react with O_2 at pH 7.0. It is proposed that the unpaired spin of the $^{\bullet}$OH adduct is delocalized to give a heteroatom-centered radical.

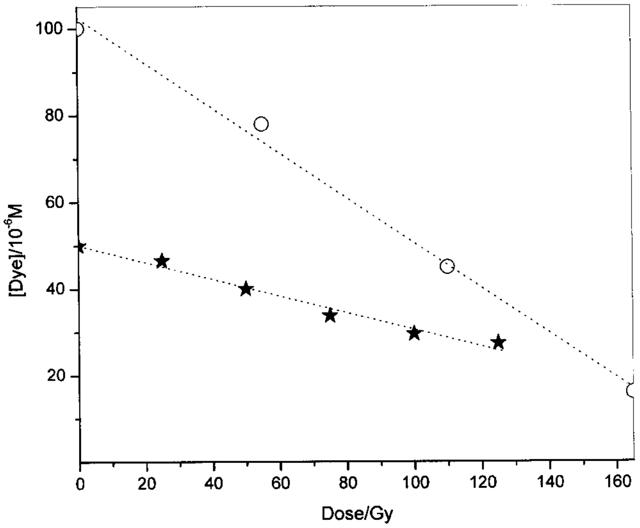


Figure 5. Dependence of the loss of unsubstituted dye on radiation dose for γ-irradiation of a N_2O-saturated, aqueous solution containing either 0.1 mM unsubstituted dye (○) or 50 μM unsubstituted dye (★) and 20 mM NaN_3 at pH 7.0.

The spectral characteristics of the species produced in the reaction of $N_3^{\bullet}$ with the dyes, determined 20−30 μs after the pulse, are shown in Figures 2A−D and 3. The transient optical

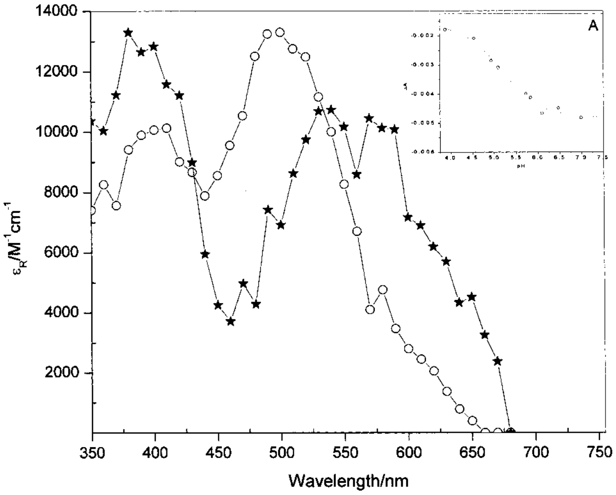


Figure 6. Corrected transient optical absorption spectra obtained in the reaction of $SO_4^{\bullet -}$ with para-methoxy-substituted dye (50 μM) at pH 4.1 (○) and at pH 7.0 (★), 20 μs after the pulse. Inset A shows the dependence of the optical absorption at 460 nm on pH. Dose/pulse = 4 Gy.

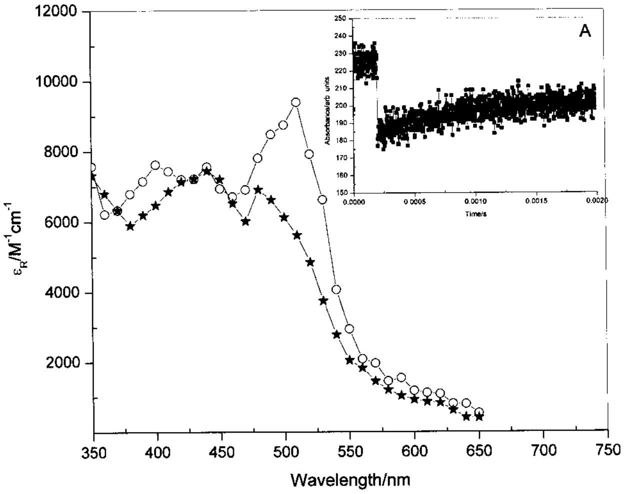


Figure 7. Corrected transient optical absorption spectra obtained 4 μs after the radiation pulse for the species produced in the reaction of e^-_{aq} (○) and $H^\bullet$ (★) with unsubstituted dye (0.1 mM) at pH 7.0. Dose/pulse = 7 Gy. Inset A shows the optical absorbance changes with time in a solution containing 50 μM of unsubstituted dye determined at 490 nm at pH 7.0. Dose/pulse = 3.8 Gy.

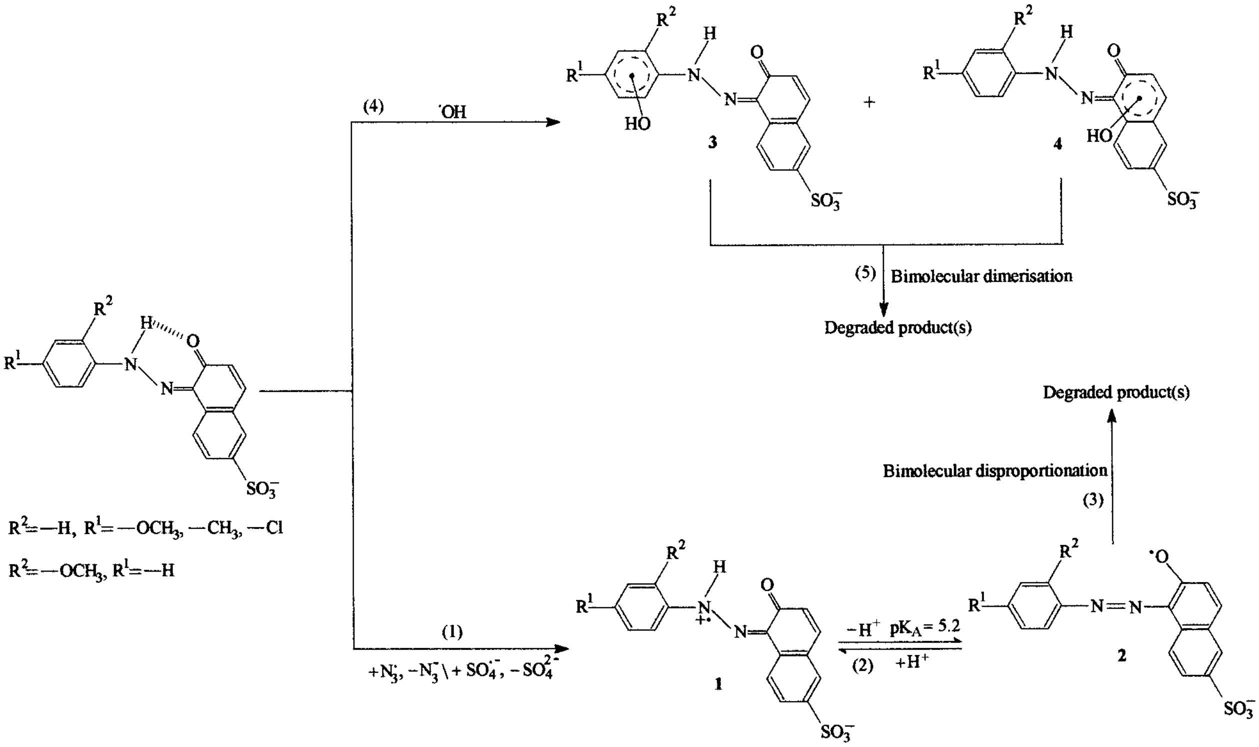
absorption spectra of the species formed on reaction of $N_3^\bullet$ with these dyes is significantly different than those induced by the $^\bullet$OH. The optical absorption spectrum of the transient species for reaction of $N_3^\bullet$ with the unsubstituted dye is identical with that reported[32] for reaction of $N_3^\bullet$ with the dye anion. The corrected transient absorption spectra for the unsubstituted, ortho-methoxy, para-methoxy, para-methyl, and para-chloro derivatives exhibit a peak at 390 nm and a broad maximum in the range 500−530 nm. The species produced in the reaction of $N_3^\bullet$ with the para-methoxy derivative at pH 7.0 (Figure 3) shows absorption maxima at 390 and 575 nm, representing a red shift with respect to that with the unsubstituted dye radical (Figure 2A). The transient optical absorption spectra are assigned to the formation of the one-electron oxidized radical of the dye. Similarly, the optical absorption spectra for the other substituted derivatives are assigned to one-electron oxidized radicals of the respective dyes. The one-electron oxidized radical of the para-methoxy derivative was also produced in its reaction with $SO_4^{\bullet -}$ at pH 4.1 and 7.0. The optical absorption spectrum for the reaction of $SO_4^{\bullet -}$ with the para-methoxy dye at pH 7.0 is identical with that of the one-electron oxidized species produced in the reaction of the dye with $N_3^\bullet$ (Figures 3 and 6). However, the optical absorption spectrum for the species produced on reaction of $SO_4^{\bullet -}$ with the para-methoxy dye at pH 4.1 is blue-shifted with respect to that observed at pH 7.0 (Figure 6). The dependence of optical absorbance of the species produced in the reaction of $SO_4^{\bullet -}$ with the para-methoxy dye on pH is shown in Figure 6, inset A. From this dependence, the pK_A of the one-electron oxidized radical of the para-methoxy derivative was determined to be 5.2 ± 0.2. The optical absorption spectrum for the reaction of $SO_4^{\bullet -}$ with the para-methoxy dye at pH 4.1 is suggested to be that of the dye radical cation.

The decay kinetics of the transient species formed in the reaction of $N_3^\bullet$ with the para-methoxy derivative at 560 nm are bimolecular with a second-order rate constant of 1.0×10^{10} M^{-1} s^{-1} determined at pH 7.0. The second-order rate constants for loss of the species produced on reaction with $N_3^\bullet$ for the other dyes are in the range $(4-10) \times 10^9$ M^{-1} s^{-1}.

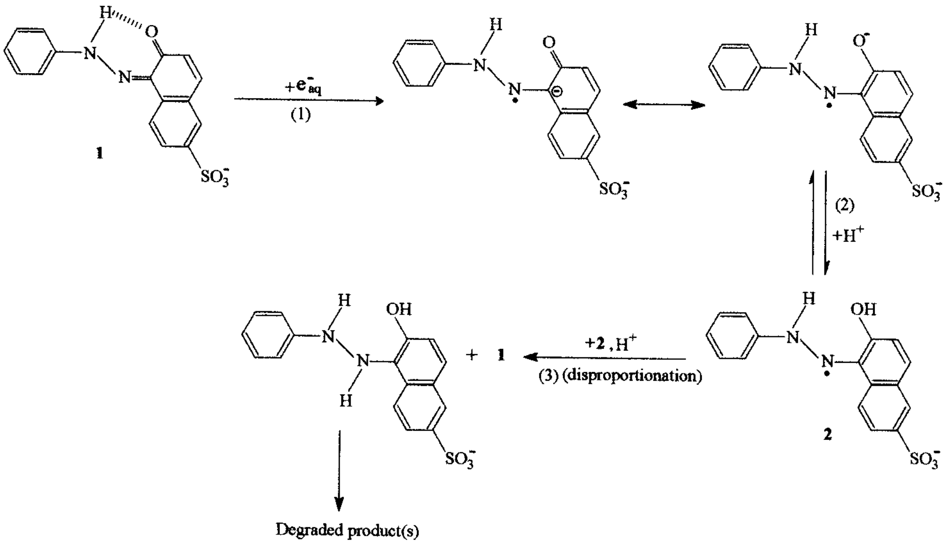
Similar to the observations for the bimolecular decay of the $^\bullet$OH adducts of the dyes, a decrease in the optical absorption at wavelengths within the visible absorption band of the ground state of the dyes is induced by reaction with $N_3^\bullet$, corresponding to decay of the resulting one-electron oxidized radicals of the dye. However in contrast to the bimolecular dimerization of the $^\bullet$OH adducts, the changes of absorbance with time (Figure 4C,D) are consistent with disproportionation of the species induced by $N_3^\bullet$ following decay of the one-electron oxidized species at 560 nm. From the pulse radiolysis data at 490 nm, 0.9 μM of the unsubstituted dye was removed for a dose that produces 2.2 μM of $N_3^\bullet$ and assuming that the product(s) of the decay of the one-electron oxidized radicals do not absorb strongly at 490 nm. Thus, the stoichiometry of the reaction with $N_3^\bullet$ removes one dye molecule per 2.4 $N_3^\bullet$. The radiation chemical yield for $N_3^\bullet$-induced loss of the unsubstituted dye was also determined following the γ-irradiation of N_2O-saturated aqueous solution containing 50 μM dye. The dependence of the decrease of absorbance with dose is linear with a slope of $(2.2 \pm 0.3) \times 10^{-7}$ M Gy^{-1}(Figure 5), corresponding to half of the yield per unit dose of $N_3^\bullet$ (5.5×10^{-7} M Gy^{-1}) assuming the absorbance of the product(s) at this wavelength is negligible. However, the optical absorbance of the product(s) is significant at 490 nm (e.g, 175 Gy is equivalent to ~90 μM of $N_3^\bullet$). If it is assumed that this absorbance is due to product(s), the dependence of the decrease of absorbance, after correction for that of product(s), with dose is linear with a slope of $(1.9 \pm 0.2) \times 10^{-7}$ M Gy^{-1}. Therefore, 2.5−2.8 $N_3^\bullet$ are required to destroy one molecule of dye, which is in agreement with bimolecular decay of the one-electron oxidized species occurring predominantly by disproportionation.

(ii) Reaction of e^-_{aq}. The corrected transient optical absorption spectrum of the species produced on reaction of e^-_{aq} with the unsubstituted dye was determined at pH 7.0 on pulse irradiation of N_2-saturated, aqueous phosphate buffer solutions containing the unsubstituted azo dye and 0.2 M 2-methylpropan-2-ol and is shown in Figure 7. With the use of the isopropyl alcohol radical as a one-electron reductant, the rate constant for reduction of the unsubstituted dye by the isopropyl alcohol radical was found to be lower by an order of magnitude ($k = 2.5 \times 10^9$ M^{-1} s^{-1}) than that with e^-_{aq} ($k = 2.5 \times 10^{10}$ M^{-1} s^{-1}). The bimolecular decay of the electron adduct of the dye was confirmed from the inverse proportionality of the first half-life of the species with the dose/pulse used (3−9 Gy). Similar to the one-electron oxidized dye, the electron adducts undergo

SCHEME 2: Reaction Pathways of $^{\bullet}OH$, $N_3^{\bullet}$, and $SO_4^{\bullet -}$ with the Azo Naphthol Dyes



SCHEME 3: Reaction Pathways of e^{-}_{aq} with the Azo Naphthol Dyes



bimolecular decay, preferentially by disproportionation, as inferred from the change of absorbance at 490 nm after completion of the disappearance of the electron adducts (Figure 7, inset A). The initial loss of the dye at 490 nm is due to the reaction of e^{-}_{aq} with the unsubstituted dye followed by partial restoration of the absorbance. The concentration for loss of unsubstituted dye was determined to be 0.4 μM for a radiation dose that produces ~1 μM (3.8 Gy) of e^{-}_{aq}. Therefore, ~2.5 μM of e^{-}_{aq} are required to remove ~1 μM of the dye. The second-order rate constant for decomposition of the electron adduct of the unsubstituted dye at pH 7.0 is 2.1×10^{10} M^{-1} s^{-1}.

The corrected transient absorption spectrum of the H atom adduct of the dye was also determined at pH 1.0, at which e^{-}_{aq} is quantitatively converted into $H^{\bullet}$ by reaction with protons. The spectrum of the H atom adduct of the unsubstituted dye determined at pH 1.0 is different from that of the one-electron reduced species produced at pH 7.0 (Figure 7).

(c) Reaction Mechanism. The reaction mechanisms are discussed on the basis of the dye reactive form being the hydrazone tautomer.

(i) Reaction with $N_3^{\bullet}$ and $SO_4^{\bullet -}$. Because $N_3^{\bullet}$ and $SO_4^{\bullet -}$ generally react by direct electron transfer, the formation of the radical cation **1** (reaction 1) is proposed in the first step as shown in Scheme 2. The dependence of the rate constants for reaction of $N_3^{\bullet}$ with the substituted dyes at pH 7.0 upon the substituent is consistent with electron transfer. The radical cation subsequently undergoes a prototropic equilibrium (reaction 2). If pH > pK_A of the dye radical, it deprotonates to the corresponding dye radical **2**, on the basis of the similarity of its spectrum at pH 7.0 with that reported[32] in the reaction of $N_3^{\bullet}$ with the dye at pH 12 (common anion).

The dye radical **2** subsequently decays bimolecularly by disproportionation at pH 7.0 (reaction 3), resulting in loss of absorbance in the visible region of the absorption spectrum of the dye. This mechanism is similar to that proposed for the bimolecular degradation of the dye proposed by Coen et al.[32] in their recent study of the reaction of $N_3^•$ with the dye common anion and the findings based on peroxidase-mediated dye oxidation.[14] The important finding of the present study is that the one-electron oxidized dye radical leads to decolorization of solutions even in neutral solution.

(ii) Reaction with $^•$*OH.* The $^•$OH generally reacts by addition or H abstraction or both. Considering the rate constants for reaction of $^•$OH with the dye ($k = 1 \times 10^{10}$ M^{-1} s^{-1}), direct H abstraction from the β- nitrogen, the rate of which is expected to be lower than that of addition by 1 or 2 orders of magnitude, is considered unlikely. Because the rate constant for the reaction of $^•$OH with the dyes is unaffected by the substituent, it is proposed that the first step in the reaction of $^•$OH is addition to either the benzene ring or the naphthol ring (reaction 4, Scheme 2), forming the corresponding $^•$OH adducts **3** and **4**. Preference for $^•$OH addition to the naphthol group with the unsubstituted dye is supported by the low reactivity of the $^•$OH adduct of the unsubstituted dye with O_2. Addition of $^•$OH to the benzene ring would yield a carbon-centered radical, which is expected to react with oxygen. Addition of $^•$OH to the naphthol ring results in radicals in which the radical site may be delocalized to the heteroatoms, which are not generally that reactive with oxygen. The $^•$OH adducts of benzene derivatives[33] and naphthols[33] are known to absorb in this region. The lack of observation of dehydration reactions of the $^•$OH adducts is consistent with the optical absorption spectra of the species produced in the reaction of the dyes with $^•$OH and $N_3^•$ being different. Another confirmatory test for the formation of $^•$OH adducts was carried out by recording the transient optical absorption spectra in N_2O-saturated solutions of the unsubstituted dye (0.1 mM) in the presence of 0.05 mM reductant TMPD (*N*,*N*,*N*′,*N*′-tetramethyl-1,4-diphenylenediamine). No delayed growth at 610 nm due to the formation of $TMPD^{•+}$ was seen, because the dye radical cation, if formed, would be expected to oxidize TMPD, on the basis of their known redox potentials. The $^•$OH adducts decay bimolecularly to produce predominantly dimers at pH 7.0 and hence bleaching of the dyes. The stoichiometry of the reaction corresponds to one $^•$OH removes one dye molecule.

(iii) e^-_{aq} *Reaction.* The e^-_{aq} is expected to react with the heteroatom leading to formation of the radical anion (reaction 1). The e^-_{aq} adds to the sp^2-hybridized N atom attached to the naphthol moiety of the unsubstituted dye **1** giving rise to the dye radical anion (electron adduct) as shown in Scheme 3. The initially formed radical anion is protonated very fast by water[44] leading to the formation of hydrazyl radical **2** (reaction 2). The hydrazyl radical **2** further decays bimolecularly, predominantly by disproportionation, to give **1** and product(s) (reaction 3), which are unstable and subsequently degrade to aromatic amines.[23,30g]

The difference seen between the optical absorption spectra of the electron adduct and the H atom adduct probably reflects addition of the H atom to the naphthyl or phenyl moiety or both to produce carbon-centered radicals.

Conclusions

The oxidation of a series of arylazo naphthol dyes by $^•$OH proceeds by addition giving rise to $^•$OH adducts. In contrast, the reaction of $N_3^•$ is more selective, proceeding by one-electron oxidation to produce the one-electron oxidized dye radical, which for the para-methoxy derivative has a pK_A of 5.2. The one-electron oxidized radicals decay bimolecularly, predominantly by disproportionation, whereas the dye radicals induced by $^•$OH at neutral pH decay by bimolecular dimerization. Reduction of the dyes by e^-_{aq} leads to the formation of a hydrazyl radical, which decays also bimolecularly by disproportionation. The $^•$OH-radical-induced dimerization of the dyes represents the more efficient method of decolorizing the dyes.

Acknowledgment. The financial support from IUC-DAEF, CC, in the form of a grant-in-aid in carrying out this work is gratefully acknowledged. K.K.S. thanks Unilever Port Sunlight laboratory, U.K., for a short-term fellowship and the Radiation and Genome Stability Unit, MRC, Harwell, U.K., for providing the laboratory facilities.

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