JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 221–226 (1999)

Hydroxyl radical-induced oxidation of azo dyes: a pulse radiolysis study

Sarojini Padmaja and Stephen A. Madison*

Organic Division, Unilever Research US, 45 River Road, Edgewater, New Jersey 07020, USA

Received 13 May 1998; revised 9 July 1998; accepted 14 July 1998

ABSTRACT: The hydroxyl radical ($^{\bullet}OH$)-mediated oxidation of two simple textile azo dyes, methyl orange and calmagite, was studied by the pulse radiolysis technique. The oxidation of methyl orange and calmagite by hydroxyl radicals was extremely fast, with second-order rate constants of $(2.0 \pm 0.3) \times 10^{10}$ and $(1.1 \pm 0.2) \times 10^{10}$ l mol^{-1} s^{-1}, respectively, at 25 °C and pH 9.2. The transient intermediates formed by the interaction of hydroxyl radical with the dyes displayed absorption bands at 300, 480 and 720 nm for calmagite and 360 and 580 nm for methyl orange. These transients decompose by first-order kinetics with half-lives of 150–200 μs. In the case of methyl orange, hydroxyl radical reacts by one-electron oxidation at the nitrogen center, forming the anilino cation radical. This was confirmed by comparing the absorption spectrum of the intermediate formed by the interaction of $^{\bullet}OH$ with methyl orange and that obtained by the reaction between a one-electron oxidant such as carbonate radical ($CO_3^{-\bullet}$) and methyl orange. Hydroxyl radicals react with calmagite by addition to the benzene ring, producing hydroxycyclohexadienyl radicals, which rapidly decompose to phenoxyl-type radicals by water elimination. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: azo dyes; oxidation; hydroxyl radical; pulse radiolysis

INTRODUCTION

Azo dyes are synthetic organic dyes that are used in the textile, cosmetic, paper, drug and food processing industries. They are designed to be adherent, long lasting and resistant to chemical processes. However, it is essential that these dyes be removed from industrial effluents and several methods such as degradation by treating with one-electron oxidants[1–3] and photocatalytic processes[4–6] have been employed. Hydroxyl radicals were extensively used as primary oxidants in advanced oxidation processes for the degradation of organic pollutants[2,3] and textile dyes[7,8] from industrial wastes owing to their high reactivity. On the other hand, in the case of dyed fabrics it is required that the dyes should not fade through oxidation in the normal washing processes.[9,10] In any case, a detailed understanding on the kinetics and mechanism of the oxidation of textile dyes by one-electron oxidants is important. The reaction of hydroxyl radical with azobenzene,[11] the simplest of azo dyes, is reported to be a diffusion-controlled reaction with a rate constant of 2×10^{10} l mol^{-1} s^{-1}. There are no reports in the literature on the reaction of methyl orange and calmagite with hydroxyl radicals. In order to understand the mechanism of oxidation of textile azo dyes by hydroxyl radical, we selected methyl orange and calmagite as model compounds for the present investigation. With the pulse radiolysis technique, one can selectively generate oxidizing or reducing species from radiolysis of water.[12–15] Thus in neutral or alkaline solutions, the interaction of high-energy electrons with water molecules leads to the production of hydroxyl radicals and hydrated electrons in equal yields. By scavenging aqueous electrons with suitable scavengers such as N_2O, one can produce the hydroxyl radical as the ultimate reacting species. Hydroxyl radical in water exhibits a very weak optical absorption at 230 nm (Σ_{230} = 665 l mol^{-1} cm^{-1}), with the result that its reactivity cannot be determined by direct observation.[16] In the presence of added substrates, the reaction of hydroxyl radicals with the substrate can be studied by optical absorption spectroscopy either by competition kinetics[17] or by following the product build-up.[18] Here we report the results of our investigation on the oxidation of two model azo dyes by pulse radiolytically generated hydroxyl radicals. The kinetics, nature of the transients formed and the mode of reaction of hydroxyl radical with methyl orange and calmagite are discussed.

EXPERIMENTAL

Materials and methods. Methyl orange and calmagite

**Correspondence to:* S. A. Madison, Organic Division, Unilever Research US, 45 River Road, Edgewater, New Jersey 07020, USA.
E-mail: Stephen.a.madison@unilever.com

CCC 0894–3230/99/030221–06 $17.50

were purchased from Aldrich Chemical (Milwaukee, WI, USA). Buffer solutions were prepared by literature methods and Milli-Q water was used for preparing all solutions. Solutions were prepared freshly and saturated with N_2O before irradiation. The solutions were allowed to flow through an irradiation cell with a 2 cm optical pathlength perpendicular to the electron beam. The flowrate was sufficient to replenish the solution in the cell between pulses. All experiments were performed at room temperature. Absorption spectra were recorded using a Hewlett-Packard Model 8645 diode-array spectrophotometer.

Pulse Radiolysis. Pulse radiolysis experiments were conducted at the National Institute of Standards and Technology (Gaithersburg, MD, USA). We used a Febetron 705 accelerator supplying 50 ns pulses of 2 MeV electrons as the source for water radiolysis. The dose per pulse was usually 5 Gy, determined using KSCN dosimetry. For optical detection we used a Varian 300 W xenon lamp separated from the cell by a shutter, and a monochromator and photomultiplier located in a separate room from the irradiation region. Reactions were followed by monitoring the build-up of the product absorption. For kinetic studies, reactions were carried out under pseudo-first-order conditions with respect to the substrate. The kinetic traces were digitized by using a Tektronix Model 7612 transient recorder and processed by a computer. Second-order rate constants were determined from the slope of the plots of pseudo-first-order rate constants *vs* concentration of the substrate. Time-dependent absorption spectra were measured by monitoring the absorbances of the transients at different wavelengths.

RESULTS

Reaction of hydroxyl radical with calmagite

Hydroxyl radicals were generated by the pulse radiolysis of an N_2O-saturated aqueous solution:

$$H_2O \rightarrow {}^{\cdot}OH, e^-_{aq}, {}^{\cdot}H, H_2O_2, H_2, H_3O^+ \qquad (1)$$

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + {}^{\cdot}OH + OH^- \qquad (2)$$

The rate constant for reaction (2) is diffusion controlled ($k_2 = 9.8 \times 10^9\,l\,mol^{-1}\,s^{-1}$)[19] such that in N_2O-saturated solutions all hydrated electrons (e^-_{aq}) formed will be quantitatively converted to hydroxyl radicals. The electronic absorption spectrum and the molecular structure of an aqueous solution of calmagite at pH 9.5 are shown in Fig. 1. The chromophoric absorption for calmagite has a maximum at 605 nm with a molar absorptivity of $\Sigma = 20{,}300\,l\,mol^{-1}\,cm^{-1}$.[20] Pulse radiolysis of an N_2O-saturated aqueous solution containing 20 μM calmagite at pH 9.5 resulted in the rapid formation of a transient with the absorption spectrum shown in Fig. 2. It exhibits absorption bands at 300 and 720 nm with a shoulder at 480 nm. The strong negative absorption at 600 nm is due to the bleaching of the dye. The bleaching maximum corresponds to the ground-state absorption maximum of the dye (Fig. 1). The absorptions at both 300 and 720 nm decay by first-order kinetics with an overall lifetime of 150 μs. The second-order rate constant for the reaction between calmagite and hydroxyl radical was determined from the build-up of the transient absorption at 300 nm to be $(1.1 \pm 0.2) \times 10^{10}\,l\,mol^{-1}\,s^{-1}$.

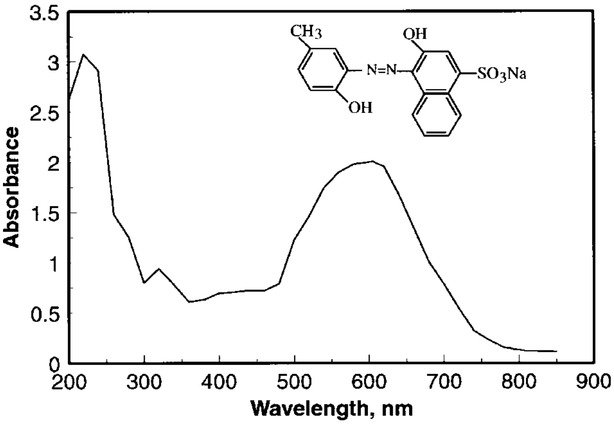


Figure 1. Molecular structure and electronic absorption spectrum of an aqueous solution containing 100 μM calmagite at pH 9.5

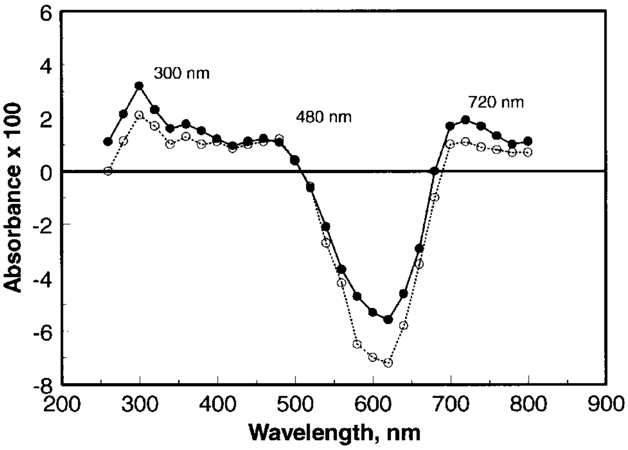


Figure 2. Time-resolved absorption spectrum of the transient obtained on the pulse radiolysis of an aqueous N_2O saturated solution of calmagite (20 μM) at pH 9.5. The pH of the solutions was maintained using 10 mM borate buffer. The solid line represents the spectrum at 2 μs after the pulse and the dotted line at 20 μs after the pulse

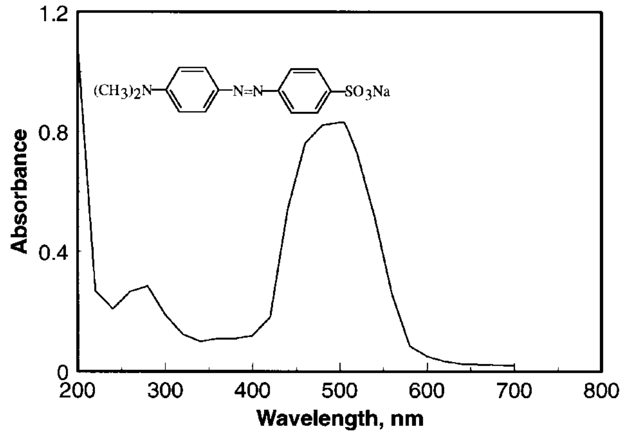


Figure 3. Molecular structure and electronic absorption spectrum of an aqueous solution containing 40 μM methyl orange at pH 9.5

Reaction of hydroxyl radical with methyl orange

Figure 3 shows the molecular structure and electronic absorption spectrum of methyl orange at pH 9.5. The transient absorption spectrum of the intermediate produced in the pulse radiolysis of an N_2O-saturated aqueous solution of methyl orange (20 μM) at pH 9.2 is shown in Fig. 4. The absorption spectrum shows maxima at 360 and 580 nm with bleaching at 500 nm corresponding to the ground-state absorption of methyl orange. At longer times, the transient absorptions at both 360 and 580 nm decayed by first-order kinetics to stable products with a rate constant of 5.6×10^3 s^{-1}.

The kinetics of the reaction between ˙OH and methyl orange were monitored by following the build-up of the transient absorption at 580 nm. The reaction was found to have a second-order rate constant of $(2.0 \pm 0.3) \times 10^{10}$ l mol^{-1} s^{-1} at 25 °C, approximately twice that obtained for calmagite. These pulse radiolysis studies characterize the initial reaction steps between ˙OH radical and methyl orange.

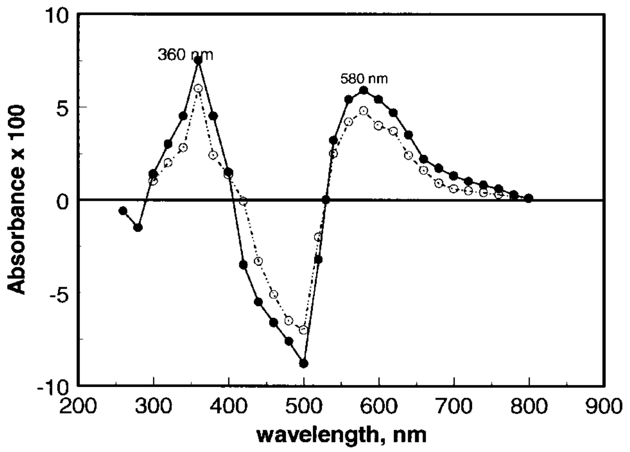


Figure 4. Time-resolved absorption spectrum of the transient obtained on the pulse radiolysis of an N_2O saturated aqueous solution of 20 μM methyl orange at pH 9.2. The pH of the solutions was maintained using 10 mM borate buffer. The solid line represents the spectrum at 4 μs after the pulse and the dotted line at 30 μs after the pulse

The hydroxyl radical is an unselective radical and reacts with substrates by multiple mechanisms such as electron transfer, addition and hydrogen abstraction.[21–23] Therefore, it is possible that the transient intermediates observed in the case of calmagite and methyl orange could be an OH adduct or a one-electron oxidation product of the dye, or both. In order to understand the nature of the transient intermediate from ˙OH with methyl orange, we decided to compare the reactivities of a known one-electron oxidant and hydroxyl radical towards this dye. For this purpose, we selected carbonate radical, which is known to react with aromatic compounds by one-electron transfer.[24] Further, carbonate is a major contaminant in wastewaters,[25] and in any advanced oxidation processes the primarily formed hydroxyl radical could react with natural source of carbonate in water to form the carbonate radical anion. For textile dyeing effluents where the pH is much greater than neutral, scavenging of ˙OH radicals by carbonate ion will be a major pathway. Hence the carbonate radical could contribute significantly to the degradation of organic pollutants, including azo dyes. Therefore, understanding the reactivity of carbonate radical towards dyes and other organic pollutants could provide new insights into the development of efficient advanced oxidation processes for wastewater treatment.

Carbonate radicals

Carbonate radicals were generated by the pulse radiolysis of an aqueous solution of 0.1 M sodium carbonate[26] at pH 11.0 according to Eqn. 3. Carbonate radical has a reduction potential of 1.6 V[27] and can be detected by its well resolved absorption spectrum with λ_{max} at 600 nm.[28]

$$^{\cdot}OH + CO_3^{2-} \rightarrow {}^{-}OH + CO_3^{-\cdot} (k_3 = 3.9 \times 10^8 \text{l mol}^{-1}\text{s}^{-1})^{17} \qquad (3)$$

The formation of the carbonate radical anion was confirmed by a transient, with an absorption maximum at 600 nm, very similar to the absorption spectrum of carbonate radical reported in the literature.[28] The study was carried out at pH 11.0 since the reaction of ˙OH with carbonate ion is much faster than that with hydrogencarbonate ion (8.5×10^6 l mol^{-1} s^{-1}).[17] The carbonate radical exists in equilibrium with the less reactive hydrogencarbonate radical, $HCO_3^{\cdot}$, [Eqn. 4] with a pK_a of 9.6.[29] Therefore, at pH 11.0 the reactive species in solution is predominantly the carbonate radical anion. Thus formed, the carbonate radical decayed by second-order kinetics with a rate constant of 1.2×10^7 l mol^{-1} s^{-1} at 25 °C.

$$HCO_3^- \rightleftharpoons CO_3^{-\cdot} + H^+ (pK_a = 9.6) \qquad (4)$$

Reactions of $CO_3^{-\cdot}$ with methyl orange

The reaction of carbonate radical with methyl orange was studied at pH 11.0 and 25 °C. The kinetics were followed by monitoring the decay of carbonate radical at 600 nm. In the presence of methyl orange, the apparent carbonate radical decay at 600 nm did not go to zero absorption owing to its reaction with the dye and subsequent formation of a transient having absorption in the same range where $CO_3^{-\cdot}$ absorbs. The initial decay of carbonate radical at 600 nm was analyzed to extract the pseudo-first-order rate constants at different initial concentrations of methyl orange. The second-order rate constant for the reaction between carbonate radical and methyl orange at pH 11.0 was determined to be $(2.1 \pm 0.3) \times 10^8$ l mol^{-1} s^{-1}, which is two orders of magnitude lower than that of the reaction of hydroxyl radicals with methyl orange (2.0×10^{10} l mol^{-1} s^{-1}).

The transient absorption spectrum of the intermediate formed in the reaction between carbonate radicals and methyl orange was determined by measuring the absorbance over the wavelength range 300–800 nm. Since the rate constant for the reaction between methyl orange and carbonate radicals is low, a high concentration of the dye (0.2 mM) was used to obtain a measurable concentration of the transient intermediate. Owing to this high dye concentration, the analyzing light intensity was close to zero in the wavelength region from 380 to 500 nm, making it impossible to measure the transient absorption in this region. Figure 5 shows the transient absorption spectrum obtained in the pulse radiolysis of an aqueous solution of 0.1 M carbonate in the presence of 0.2 mM methyl orange at pH 11.0. This absorption spectrum exhibits maxima at 360 and 580 nm with an absorbance ratio (A_{360}/A_{580}) of 1.2. The carbonate radical is a one-electron oxidant and therefore the absorption spectrum shown in Fig. 5 should be that of the one-electron oxidation product of methyl orange, the anilino cation radical. If one compares Fig. 5 with Fig. 4 (spectrum of the transient from $^{\cdot}$OH with methyl orange), the absorption spectrum shows the same maxima in either case and also the ratio of the absorbance between 360 and 580 ($A_{360}/A_{580} = 1.2$) is identical. This suggests that the same intermediate is formed in the reactions of $^{\cdot}$OH and $CO_3^{-\cdot}$ radicals with methyl orange.

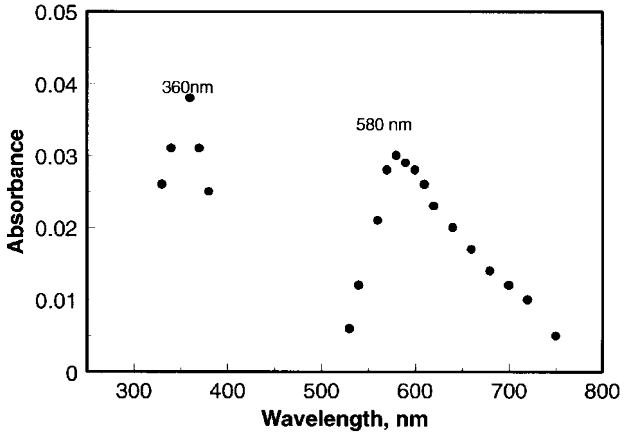
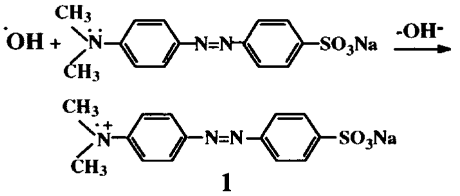


Figure 5. Transient optical absorption spectrum obtained on pulse radiolysis of an N_2O-saturated aqueous solution containing 0.1 M carbonate and 0.2 mM methyl orange at pH 11.0. The absorbances were measured at 30 μs after the pulse

DISCUSSION

The hydroxyl radical-induced oxidation of two model textile azo dyes, calmagite and methyl orange, was studied by the pulse radiolysis technique. The reactions of hydroxyl radicals with these azo dyes are diffusion controlled with rate constants of 1.1×10^{10} and 2.0×10^{10} l mol^{-1} s^{-1}, respectively, at 25 °C. These rate constants are in good agreement with that of 2.0×10^{10} l mol^{-1} s^{-1} reported[11] for the reaction of $^{\cdot}$OH with azobenzene, the simplest model for an azo dye. In the reaction of hydroxyl radicals with methyl orange, a transient intermediate is observed immediately after the reaction which decomposes to stable products at longer times. The rate (rate constant × concentration) of $^{\cdot}$OH radicals reacting with methyl orange is 4.0×10^5 s^{-1} under the experimental conditions used in Fig. 2. This value is much higher than the rate of self decay of $^{\cdot}$OH radicals (4.2×10^4 s^{-1}), suggesting that all the $^{\cdot}$OH radicals have reacted with methyl orange. Hydroxyl radicals are known to add to the benzene ring to form hydroxycyclohexadienyl radicals absorbing in the region 300–320 nm.[30,31] Since methyl orange has a dimethylamino group, this will be the most likely site of oxidation by the hydroxyl radical. Hydroxyl radicals could attack the dimethylamino group of methyl orange by abstracting a methyl hydrogen, forming *N*-methylanilinomethyl radical. The hydrogen abstraction reactions of $^{\cdot}$OH from substituents are usually one to two orders of magnitude slower than that of addition and electron transfer reactions.[17] The high rate constant for the reaction of $^{\cdot}$OH with methyl orange (2.0×10^{10} l mol^{-1} s^{-1}) observed in the present case strongly argues against the possibility of hydrogen atom abstraction. However, such hydrogen atom abstraction reactions leading to the formation of anilinomethyl radical (30% yield) is observed in the reaction of $^{\cdot}$OH with *N*,*N*-dimethylaniline with the other 70% resulting in the one-electron oxidation product.[21] Given this possibility, reaction of $^{\cdot}$OH with methyl orange can also be expected to occur by a mixed transient formation. If the absorption spectrum shown in Fig. 4 is due to a mixture of transients, the rate at which the absorptions at 360 and 580 nm decay would be different. However, the transient absorptions at 360 and 580 nm decayed with the same rate constant and additionally the ratio of the absorbances at 360 to 580 nm at different times was found to be the same. Therefore, this suggests that in the reaction of ˙OH with methyl orange only one transient is formed. The nitrogen of the dimethylamino group of methyl orange is highly electron rich, making it more susceptible to attack by the radical through one-electron transfer [Eqn. 5]. Hence the absorption espectrum shown in Fig. 2 should be that of the anilino cation radical (**1**).

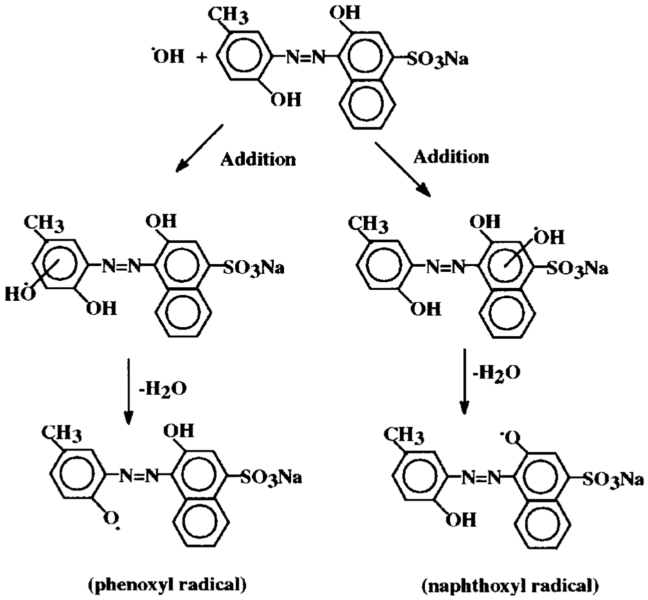


1

(5)

In order to confirm this, we studied the reaction of methyl orange with a known one-electron oxidant such as carbonate radical. The reaction between methyl orange and carbonate radical produced a transient with an absorption spectrum (Fig. 5) similar to that obtained from the reaction of ˙OH with methyl orange (Fig. 4). Further, the ratio of the absorbances at 360 to 580 nm is 1.2, suggesting that in either case these are the same transient intermediates. Therefore, the results strongly suggest that hydroxyl radical reacts with methyl orange by one-electron transfer to produce the cation radical as the immediate product of the reaction. The cation radical thus formed has a lifetime of 180 μs and decomposes to stable products at longer times.

Calmagite is an *o,o*′-dihydroxy azo dye which can exist in either one of two tautomeric forms,[32] an azo form or a hydrazone form, or an equilibrium mixture of both, depending on the pH. The pK_a values of the naphtholic and phenolic OH groups of calmagite are 8.14 and 12.35, respectively.[33] In the present study, since the reactions were carried out at pH 9.5, it is possible that calmagite exists predominantly in the azo form. Hydroxyl radicals can react with calmagite through multiple pathways owing to the presence of different reactive sites. One-electron oxidation of the phenolic and naphtholic OH groups gives the phenoxyl and naphthoxyl radicals, respectively, which typically absorb near 400 nm.[34] Addition to the benzene ring produces hydroxycyclohexadienyl radicals with absorption in the range 300–320 nm. The reaction of hydroxyl radical with phenol leading to the formation of phenoxyl radical has been reported by Land and Ebert.[34] They proposed a mechanism involving the formation of an ˙OH adduct of phenol as the initial step, followed by rapid water elimination generating the phenoxyl radical. However, Field *et al.*[35] reported that in the reaction of ˙OH with phenol a substantial amount of direct hydrogen abstraction from the phenolic OH group also occurs, leading to the formation of phenoxyl radical. The rate constant for the reactions of ˙OH with phenol and 2-naphthol are 1.4×10^{10} and 1.2×10^{10} l mol^{-1} s^{-1}, respectively,[17,36] close to that obtained for the reaction of ˙OH with calmagite. Since calmagite has both naphtholic and phenolic OH groups, the interaction with hydroxyl radical could produce a mixture of phenoxyl- and naphthoxyl-type radicals or possibly the naphthoxyl in preference to the phenoxyl (the reduction potential of naphthol is lower than that of phenol). It is also known that the decomposition of the initial OH adducts of phenol to form phenoxyl radical is catalyzed by both bases and buffers.[34] In our studies, the reaction of ˙OH with calmagite was carried out at pH 9.5 in the presence of borate buffer. Therefore, it is possible that the initial OH adduct of calmagite decomposes rapidly to the phenoxyl-type radical on the time-scale during which we monitored the reaction. Thus, the absorption spectrum shown in Fig. 2 could be due to a mixture of phenoxyl and naphthoxyl radicals. Scheme 1 shows the possible intermediates that could be formed in the reaction of hydroxyl radicals with calmagite.



Scheme 1

Further mechanistic understanding of these reactions will come from identifying the end products of the reactions of hydroxyl radicals with methyl orange and calmagite. These experiments are currently under way.

Acknowledgements

The authors thank Dr Pedi Neta of the National Institute of Standards and Technology (NIST), Gaithersburg, MD, for providing the pulse radiolysis facility and for many helpful suggestions.

REFERENCES

1. M. Stiborova, B. Asfaw, E. Frei and H. H. Schmeiser, *Collect. Czech. Chem. Commun.* **61**, 962–972 (1996).
2. K. Vinodgopal and P. V. Kamat, in Environmental Application of Ionizing Radiation, edited by W. J. Cooper, R. Curry and K. O'Shea, pp. 587–599. Wiley–Interscience, New York, (1998).
3. N. H. Ince and D. T. Gonenc, *Environ. Sci. Technol.* **18**, 179–185 (1997).
4. K. Vinodgopal and P. V. Kamat, *J. Photochem. Photobiol. A* **83**, 141–148 (1994).
5. C. Nasar, K. Vinodgopal, S. Hotchandini, A. K. Chattopadhay and P. V. Kamat, *Res. Chem. Intermed.* **23**, 219–231 (1997).
6. U. Stafford, K. A. Gray and P. V. Kamat, *J. Catal.* **167**, 25–32 (1997).
7. Y.-S Li, *Arch. Environ. Contam. Toxicol.* **31**, 557–562 (1996).
8. R. Bauer and H. Fallmann, *Res. Chem. Intermed.* **23**, 341–354 (1997).
9. T. Omura, Y. Kayane and Y. Tezuka, *Dyes Pigm.* **20**, 227–246 (1992).
10. T. Omura, *Dyes Pigm.* **24**, 125–141 (1994).
11. M. S. Panajkar and H. Mohan, *Indian J. Chem., Sect. A* **32**, 25–27 (1993).
12. J. Rabani and M. S. Matheson, *J. Am. Chem. Soc.* **86**, 3175–3176 (1964).
13. L. M. Dorfman, M. C. Sauer Jr, Techniques of Chemistry, Vol. **IX**, pp. 493–546. Wiley, Chichester (1986).
14. P. Neta, R. W. Fessenden and R. H. Schuler, *J. Phys. Chem.* **75**, 1654–1656 (1971).
15. P. Neta and R. H. Schuler, *J. Am. Chem. Soc.* **97**, 912–913 (1975).
16. G. Czapski and B. H. J. Bielski, *Radiat. Phys. Chem.* **41**, 503–505 (1993).
17. G. V. Buxton, L. Clive, W. Greenstock, P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data* **17**, 513–588 (1988).
18. K. H. Schmidt, A. Bromberg and D. Meisel, *J. Phys. Chem.* **89**, 4352–4357 (1985).
19. E. Janata and R. H. Schuler, *J. Phys. Chem.* **86**, 2078–2084 (1982).
20. M. Windholz, (Ed.), Merck Index, 9th ed. Merck, Rahway, NJ (1976).
21. J. Holeman and K. Sehested, *J. Phys. Chem.* **81**, 1963–1966 (1977).
22. G. S. Jolly, G. Paraskevopoulos and D. L. Singleton, *Int. J. Chem. Kinet.* **17**, 1–9 (1985).
23. A. K. Davies, E. J. Land, S. Navaratnam, B. J. Parsone and G. O. Philips, *J. Chem. Soc., Faraday Trans. 1* 22–35 (1979).
24. T. P. Elango, V. Ramakrishnan and J. C. Kuriacose, *Proc. Indian Acad. Sci. (Chem. Sci.)* **93**, 47–52 (1984).
25. C. A. Cole and E. J. Genetelli, *Environ. Sci. Technol.* **4**, 514–517 (1970).
26. R. E. Huie, C. L. Clifton and P. Neta, *Radiat. Phys. Chem.* **38**, 477–481 (1991).
27. J. L. Weeks and J. J. Rabani, *J. Phys. Chem.* **70**, 2100–2106 (1966).
28. D. Behar, G. Czapski and I. Duchovny, *J. Phys. Chem.* **74**, 2206–2210 (1970).
29. T. E. Eriksen, J. Lind and G. Merenyi, *Radiat. Phys. Chem.* **26**, 197–199 (1985).
30. L. M. Dorfman, R. E. Buhler and A. Taub, *J. Chem. Phys.* **36**, 549–552 (1962).
31. H. Mohan, M. Mudaliar, C. T. Aravindakumar, B. S. M. Rao and J. P. Mittal, *J. Chem. Soc., Perkin Trans. 2* 1387–1389 (1991).
32. J. Oakes, P. Gratton and I. Weil, *J. Chem. Soc., Dalton Trans.* 3805–3809 (1997).
33. D. J. Pocalyko, J. L. Coope, A. L. Carchi, L. Boen and S. A. Madison, *J. Chem. Soc., Perkin Trans. 2* 117–121 (1997).
34. E. J. Land and M. Ebert, *Trans. Faraday Soc.* **63**, 1181–1190 (1967).
35. R. J. Field, M. V. Raghavan and J. G. Brummer, *J. Phys. Chem.* **86**, 2443–2449 (1982).
36. S. Kanodia, V. Madhaven and R. H. Schuler, *Radiat. Phys. Chem.* **32**, 661–664 (1988).