PAPER

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Alpha-hydroxy ketones and sunlight, a novel effluent treatment?

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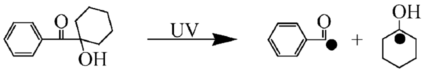
There is a need for cheap and simple methods to destroy recalcitrant pollutants such as dyes in waste water. It is shown that the radicals produced from the UV A and B photolysis of alpha-hydroxy ketones are capable of completely bleaching a wide range of azo dyes (Orange II, Amaranth, Evans Blue, Direct Green 26 and Direct Red 80). It is found that complete bleaching occurs when the ratio of [ketone]/[azo groups] is greater than 2.6–7.6 dependent on dye structure and occurs over a wide pH range (2–11 investigated). Sunlight may be used as a light source and bleaching occurs in minutes. Mechanistic investigation shows that in the presence of air the bleach reaction is predominately a 1-electron oxidation induced by the benzoyl peroxy radical. From reaction with phenols of known electropotential, the reduction potential of the benzoyl peroxy radical is estimated as ~1.9V *v* NHE. It is also shown that the benzoyl peroxy radical can undergo oxygen atom transfer reactions. In the absence of air a 1-electron reduction by the alpha-hydroxy radical [E(acetone, H^+/2-hydroxy-2-propyl) = −1.4V *v NHE*] is the main reaction. Thus the system may be switched from oxidative to reductive by removal of oxygen. Initial products are given for both oxidative and reductive routes. First cost estimates look attractive.

Introduction

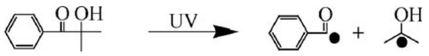
An important and active area of water chemistry is the search for cheap, simple and effective methods to destroy recalcitrant pollutants.[1–3] In this respect dyes have received attention as there are nearly one million tones of dye stuff produce globally per annum, based on more than 10 000 different structures.[4–6] Of these, azo dyes are by far the most popular class, with for example, over 80% of direct and reactive dyes being azo.[6] In many applications, once dying is complete a large amount of dye contaminated wastewater must be disposed of. Many dyes are cleverly designed to be highly stable towards light, aerobic biodegradation, and common oxidants such as hydrogen peroxide or even hypochlorite, making chemical removal extremely difficult. Physical methods, such as absorption onto activated carbon, partially removes some dyes, but leaves the problem of safe disposal of the concentrated dye.[7] A number of advanced photochemical methods have been investigated,[2] involving the production of hydroxyl radicals from hydrogen peroxide by the photo-Fenton reaction or with suspensions of semiconductors such as TiO_2. However, the photo-Fenton reaction requires undesirably high levels of iron and is restricted to low pH,[8] whilst the semiconductor route requires use of aqueous slurries which are not easy to handle. A novel photochemical alternative[9] is investigated here, involving production of reactive radicals from simple alpha-hydroxy ketones.

Alpha-Hydroxy ketones are widely used in the photocuring of coatings,[10] their photochemistry is well-investigated[11–13] and some unsubstituted derivatives are biodegradable.[14] They have a strong absorption peak at ~250–280 nm, which tails into the UVB and A. On absorption of UV light alpha-cleavage occurs producing a carbonyl and an alpha-hydroxy alkyl radical, for example 1-hydroxy-cyclohexyl-phenyl ketone (HCPK):



(1)

And 2-hydroxy-2-methyl-propiophenone (HMP)



(2)

These properties mean that highly reactive radicals can be produced on exposure to natural sunlight, *i.e.* without the need for high power lamps often used in other photodegradation methods.[1] The radicals, although not as reactive as hydroxyl ($HO^•$) or alkoxyl radicals ($RO^•$), should still be capable of bleaching and degrading pollutants, although oxygen might be expected to quench these reactions.

In this initial report, emphasis is placed on azo dyes photodestruction, as they are the most important dye class. Orange II is used a model dye,[15] and the experiments extended to the more complex poly-azo direct dyes. The ketones HCPK and HMP are employed, as they are biodegradable and hence, after aerobic biodegradation,[1] would not add to the final carbon load in the water.

Experimental

Dye/ketone solutions were made in water and placed in 1cm plastic cuvettes that were transparent to light above 300 nm. The solution were irradiated in artificial sunlight provided by an Atlas S-3000, Xenon Weather-o-meter set to give 42 W m^{-2} in the natural UV range (290–400 nm).[16] This light intensity corresponds to a sunny spring/autumn day in Northern Europe. Before and after irradiation the UV-VIS spectra of the solution were measured (1 cm path length) and the change in dye and ketone concentration calculated. In all cases degradation was completed after 30 minutes irradiation, as checked by irradiating for a further 30 minutes. For anaerobic experiments oxygen was removed by nitrogen bubbling and the solution sealed from the air to prevent re-oxygenation. Chemicals were received from commercial suppliers and all azo dyes were purified before use to remove excess salts.

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Results

Fig. 1 shows the structure of Orange II alongside the photobleaching results found with HPCK. The dye is quite photostable,[17] has a pK_a of 10.8 and exists in the unaggregated hydrazone form under current conditions.[15] In the absence of HPCK no photobleaching was observed, but on addition of small amounts a strong concentration dependent photobleaching of the dye was found, Fig. 1(a). Complete bleaching occurred at a HCPK concentration of $[\text{ketone}]_B$, and fraction $[\text{ketone}]_B/[\text{dye}]_0$ was 2.6, where $[\text{dye}]_0$ is the initial dye concentration. The ketone HMP gave analogous results with a $[\text{ketone}]_B/[\text{dye}]_0$ of 2.7. These value were independent of $[\text{dye}]_0$, Fig. 1(b).

Bleaching reactions are often strongly pH dependent, but here only very minor changes were found. When the HPCK solutions were buffered to pH 2 and 11, photobleaching also occurred, but in both cases, $[\text{ketone}]_B/[\text{dye}]_0$ slightly increased to 3.1 (not shown). Radical reaction based on carbon centered radicals such as those of reaction (1) and (2) are generally strongly influenced by oxygen, however very surprisingly removal of oxygen by nitrogen bubbling did not alter the concentration dependence or $[\text{ketone}]_B/[\text{dye}]_0$. Nonetheless, some changes were observed, for aerobic photodegradation the visible absorption spectrum simply decayed, but for anaerobic an additional peak appeared at ~410 nm, Fig 1(c). Thus different chemistries occur for anaerobic and aerobic treatment but they have the same bleaching efficiency. For aerobic treatment a strong product peak is observed at 228 nm, Fig. 1(d), which may be assigned to benzoic acid by comparison to a reference spectrum of benzoic acid. Benzoic acid is the oxidation product of the benzoyl radical, (eqns. (1) and (2)), and calibration showed that the conversion was quantitative, *i.e.* 1 mole of ketone produced 1 mole of benzoic acid after aerobic photolysis. The dye product spectrum could be obtained by subtraction of the benzoic acid peak and all these products absorbed below 300 nm.

To fully confirm that the method works with natural light a 500 ml solution of 34 micro mol L^{-1} of Orange II with 100 micro mol L^{-1} of HCPK was placed outside, on a September day in Port Sunlight. The power of the natural light was 12 W m^{-2} in UVA and 0.4 W m^{-2} in the UVB, measured using a calibrated electronic meter. Complete photobleaching of the solution was observed in 40 minutes, and no photobleaching was found with a control solution containing only Orange II.

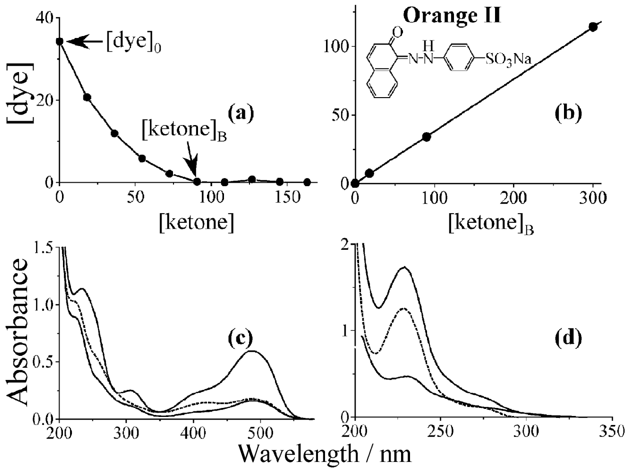


Fig. 1 (a) [Orange II] remaining in solution after irradiation verses the [ketone] added. The initial dye concentration, $[\text{dye}]_0$ is indicated as is the smallest amount of ketone, $[\text{ketone}]_B$, required for complete bleaching. All concentrations are in micro mol L^{-1}. (b) Linear dependence of $[\text{ketone}]_B$ on $[\text{dye}]_0$. (c) Absorption spectra observed after irradiation with (top) dye only, (middle, dotted) dye plus 50 micro mol L^{-1} ketone without O_2 and (bottom) dye plus 50 micro mol L^{-1} ketone with air. In all cases $[\text{dye}]_0 = 28.5$ micro mol L^{-1}. (d) UV spectrum following irradiation of: (top) 170 micro mol L^{-1} ketone plus 28.5 micro mol L^{-1} dye, (middle, dotted) 170 micro mol L^{-1} ketone and (bottom) the dye product spectrum obtained by subtraction of the other two.

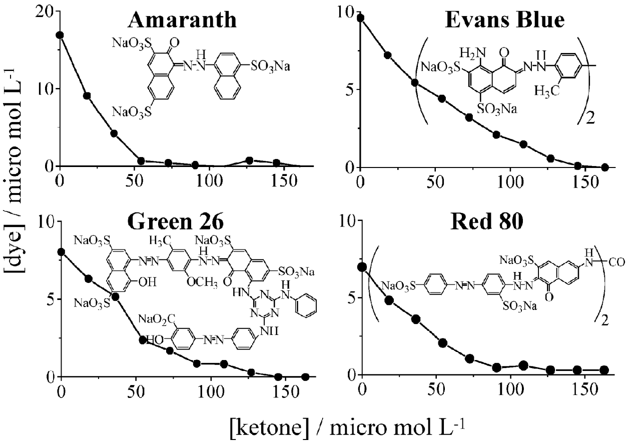
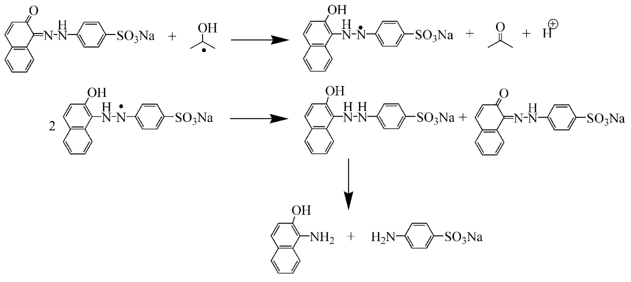


Fig. 2 Dose dependence of the photobleaching of 4 azo dyes.

To probe if the current method is applicable to a wide range of azo dyes, 4 further dyes were tested. They were chosen to contain 1 to 4 azo groups per dye, and with these groups in both hydrazone and azo form. The structures and results are given in Fig. 2 and in all cases photobleaching in the presence of the HPCK was observed. The $[\text{ketone}]_B/[\text{dye}]_0$ values were 3.2, 15.1, 16.7, 13.0 for Amaranth, Evans Blue, Green 26 and Red 80 respectively. The values per azo/hydrazone group were 3.2, 7.6, 5.6 and 3.3 respectively and are remarkably similar considering the different structural complexities. It should be noted that the technique is also very effective against reactive azo dyes.[9]

Mechanism

(i) Anaerobic bleaching. On exposure to UV light carbon centered radicals are produced in water *via* the alpha cleavage reactions shown in reaction (1) and (2). Under anaerobic conditions the reaction scheme is already relatively well-understood[18–21] and is presented in Scheme 1. The alcohol radical, *i.e.* the 2-hydroxy-2-propyl or 1-hydroxy-1-cyclohexyl radical is the active bleach species and undergoes a 1-electron reduction with the dye.[20] The 1-electron reduction potential of the (acetone, H^+/2-hydroxy-2-propyl) couple is −1.4V *v* NHE.[22] The so-produced dye radicals disproportionate to reform the dye and form a hydrazine which reacts further to give amines as the major initial products.[4,21] Due to the disproportionation, 2 alcohol radicals should be required to bleach 1 dye molecule, in reasonable agreement with the $[\text{ketone}]_B/[\text{dye}]_0$ value of 2.7. The slightly higher value observed may well be due to additional reactions of the radicals with the products.



Scheme 1 Mechanism of Anaerobic Bleaching.

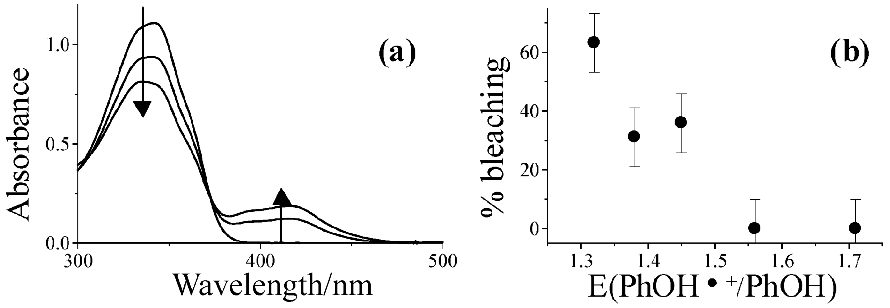
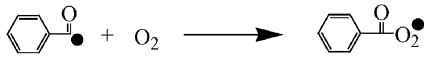
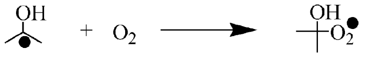


Fig. 3 (a) UV-VIS spectrum of reaction products of ABTS with HMP. The initial [ABTS] was 27 micro mol L^{-1} and the [HMP] was 0, 130 and 280 micro mol L^{-1} from top to bottom at 330 nm. (b) % Reduction in bleaching of 29 micro mol L^{-1} Orange II with 61 micro mol L^{-1} HMP in the presence of 240 micro mol L^{-1} of phenols of various potential in V *v* NHE.

(ii) Aerobic bleaching. The carbon centered radical formed from reactions (1) and (2) add to oxygen at diffusion controlled rates (k_{add} $\sim 5 \times 10^9$ mol^{-1} L s^{-1}) to give peroxy radicals, *e.g.*:[23,24]



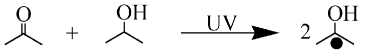
(3)



(4)

These reactions will occur in under a microsecond for normal oxygen concentrations of 280 micro mol L^{-1}. Direct dye reduction by the alcohol radicals cannot compete as although the rate constants for these reaction in water are also high, $\sim 3 \times 10^9$ mol^{-1} L s^{-1},[20,25] the concentration of dye is typically much lower. For example for Orange II, an extremely colored solution with an optical density of 1 (1 cm) corresponds to a concentration of $\sim$50 micro mol L^{-1}. Even in this extreme oxygen addition is favored by a factor of 10 over dye reduction for the alcohol radical.

To understand which of the peroxy radicals from reactions (3) and (4) were responsible for dye bleaching, the 2-hydroxy-2-propyl (2HP) radical was generated independently using acetone and propan-2-ol:[26]



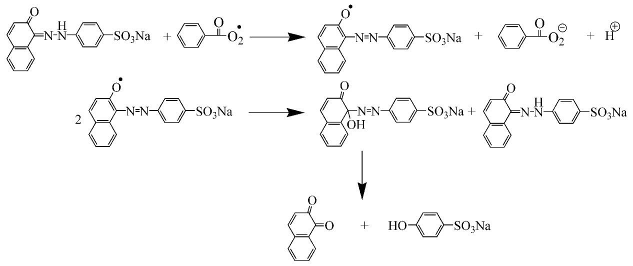
(5)

An aqueous solution containing 10% acetone, 10% propan-2-ol plus Orange II showed no bleaching on irradiation, unlike when irradiated with an alpha-hydroxy ketone. Thus the benzoyl peroxy radicals must be the active bleaching species.

Benzoyl peroxy radicals are thought to be active 1-electron oxidants.[27,28] To investigate if this reactions occurs with dyes, HMP was irradiated in the presence of 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt, ABTS, which forms a stable radical cation on oxidation that readily absorbs at 415 nm.[21,29] This cation was observed, Fig. 3(a), proving that the benzoyl peroxy radicals do act as 1-electron oxidants, *i.e.* they are readily reduced to form the benzoyl percarboxylic acid anion. To quantify the oxidative power of the radical, photoreaction was carried out at pH 7, with a series of phenols of known potential, given in Table 1.[30] In line with convention all potentials are expressed as reductions, so for the phenols the couple ($PhOH^{\bullet+}$/PhOH) is given, which is the reverse of the actual reaction. By observation of the UV-VIS spectrum, reaction was observed with the di-methyl, methyl and chlorosubstituted phenol but not the carboxylic acid or cyano. However the spectral changes were quite small, so to confirm the result a competition experiment was performed. Mixtures of Orange II, HMP, and varying concentrations of phenol were irradiated. If the phenol also reacted with the benzoyl peroxy radicals then less dye bleaching would be observed. Typical results are shown in Fig. 3(b) and in agreement with the observation on direct reaction with the phenols, only the di-methyl, methyl and chloro-subsituted phenol inhibit dye bleaching. Consequently, the benzoyl peroxy radical may 1-electron oxidise chemicals which form radicals with reduction potential up to 1.5 V *v* NHE in water. This means the benzoyl peroxy radical must have a reduction potential of 1.9 V, the 0.4 V difference being due to the solvent reorganisation energy.[31] This is a high value when compared with other oxidative systems such as enzymes, for example peroxidase enzymes which function *via* 1-electron oxidation have a potential of $\sim$0.9–1.0 V.[21]

Table 1 Electrochemical potentials of phenols

Phenol	E($PhOH^{\bullet+}$/PhOH) *v* NHE/V
3,4-methyl	1.32
4-methyl	1.38
4-chloro	1.45
4-carboxy	1.56
4-cyano	1.71



Scheme 2 Mechanism of Aerobic Bleaching *via* 1-electron oxidation.

The reaction scheme for the generic 1-electron oxidation of azo-dyes has previously been delineated and for the current case with Orange II is summarized in Scheme 2. As the reduction potential (azodye$^{\bullet+}$/azodye) is approximately 1 V,[21] they will be readily oxidized by the benzoyl peroxy radical. The so-produced dye radicals disproportionate[21] to reform the dye and form a carbenium ion which immediately hydrolyses. This product then spontaneously oxidised to form a quinone and phenol.[17] Due to the disproportionation, 2 benzoyl peroxy radicals are required to bleach 1 dye molecule, in reasonable agreement with the $[ketone]_B/[dye]_0$ value of 2.7. The slightly higher value observed may again be due to additional reactions of the radicals with the products. Further supporting this conclusion the product spectrum shown in Fig 1(d) matches the literature spectra for 1-electron oxidation products of the dye.[17] The initial quinone and phenol formed, may be further photodegraded to simple carboxylic acids.[17]

An additional possible reaction route for the benzoyl peroxy radical is that it may undergo an oxygen atom transfer reaction with the dye. A probe dye for this reaction is methyl orange, which on oxygen atom transfer forms an N-oxide which

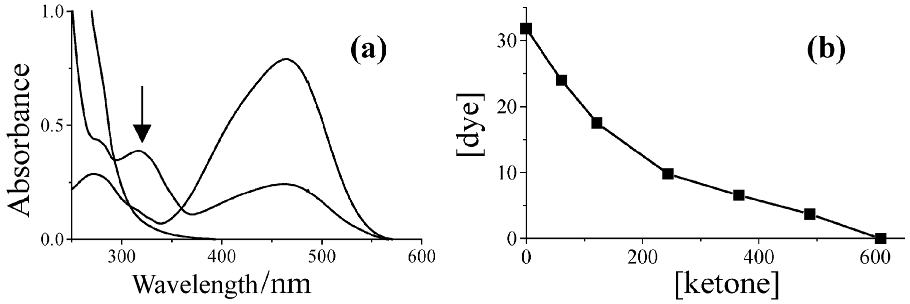
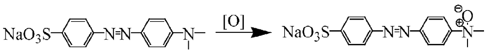


Fig. 4 (a) UV-VIS spectrum of reaction products of Methyl Orange with HMP. (a) The initial [Methyl Orange] was 32 micro mol L^{-1} and the [HMP] was 0, 240 and 605 micro mol L^{-1} from top to bottom at 460 nm. The N-oxide product is indicated with an arrow. (b) Dose dependence of bleaching of Methyl Orange with HMP. All concentrations are in micro mol L^{-1}.

absorbs at 320 nm,[21] reaction (6).



(6)

The spectra obtained from photoreaction of Methyl Orange with HMP are shown in Fig 4(a) and the oxygen atom transfer product is observed when the dye is partially bleached. Consequently the benzoyl peroxy radical can also react *via* oxygen atom transfer. The $[\text{ketone}]_B/[\text{dye}]_0$ values for Methyl Orange is 19, Fig 4(b), much higher than that observed for Orange II, therefore it appears that electron transfer is the predominant bleach route for azo-dyes. It should be noted that the major products of oxygen atom transfer bleaching of simple azo-dyes have been shown to be similar to that from 1-electron oxidation.[32]

Conclusion

The use of alpha-hydroxy ketones is an efficient method to bleach/degrade a wide range of azo dye effluent. Quite unexpectedly, the method functions equally well under aerobic and anaerobic conditions, with a corresponding simple switch from oxidative to reductive chemistry. The reason for this is that the dye radicals formed by 1 electron reduction and oxidation both decay by disproportion giving the routes the same efficiency, although obviously different products.

The method has several advantages: simplicity, as the ketone must be simply added to the effluent mixed and irradiated; there is no sludge production and it functions over a wide range of pH. First cost estimates indicate it is competitive to, or cheaper, than the other competitive systems such as membrane filtration, chemical precipitation, adsorption with activated carbon or wet air oxidation.[33,34] Clearly more work is required to fully understand the products formed and how biodegradable they are. It is known that the ketone products are biodegradable[14] and it might also be expected for many of the dye photoproducts. Hence combination of the current method with biodegradation could remove the colour from the water and lower the carbon load. Finally, the full potential of the method needs exploration as for example, initial experiments with pyrene, a polyaromatic hydrocarbon, showed strong degradation suggesting the method may have wider application than dyes.

Acknowledgements

Prof. John Oakes (Unilever Research) is thanked for useful discussions.

References

1 P. Pitter and J. Chudoba, *Biodegradability of Organic Substances*, CRC Press, Boca Raton, 1990.
2 M. M. Halmann, *Photodegradation of Water Pollutants*, CRC Press, Boca Raton, 1996.
3 L. Lave and H. J. Gruenspecht, *J. Air Waste Mange Assoc.*, 1991, **41**, 680.
4 K. Hunger, *Industrial Dyes: Chemistry Properties And Applications*, Wiley-VCH, Heidelberg, 2003.
5 T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, 2001, **77**, 247.
6 J. Shore, *Colorants and Auxiliaries Vol 1. Colorants*, Society of Dyers and Colourists: Bradford, 1990.
7 T. Robinson, B. Chandran and P. Nigam, *Water Res.*, 2002, **36**, 2824.
8 J. Fernandez, J. Bandara, A. Lopez, P. Buffat and J. Kiwi, *Langmuir*, 1999, **15**, 185.
9 S. N. Batchelor, D. A. Carr, R. J. Crawford and L. Fairclough, Patent Int. Publication No. WO 01/44127.
10 H. F. Gruber, *Prog. Polym Sci.*, 1992, **17**, 953.
11 J. P. Fouassier, D. Ruhlmann, B. Graff, F. Morlet-Savary and F. Wieder, *Prog. Org. Coatings*, 1995, **25**, 235.
12 S. Jockusch, M. S. Landis, B. Freiermuth and N. J. Turro, *Macromolecules*, 2001, **34**, 1619.
13 S. N. Batchelor and A. I. Shushin, *Appl. Mag. Res.*, 2002, **22**, 47.
14 Ciba Speciality Chemicals, Irgacure 184, Material Safety Data Sheet.
15 J. Oakes and P. Gratton, *J. Chem. Soc. Perkin Trans. 2*, 1998, 1857.
16 D. R. Lide, ed., *Handbook of Chemistry and Physics*, p 14-8, CRC Press, Boca Raton, 1992.
17 J. Bandara and J. Kiwi, *New J. Chem.*, 1999, **23**, 717.
18 K. K. Sharma, B. S. M. Rao, H. Mohan, J. P. Mittal, J. Oakes and P. O'Neill, *J. Phys. Chem. A*, 2002, **106**, 2915.
19 K. K. Sharma, P. O'Neill, J. Oakes, S. N. Batchelor and B. S. M. Rao, *J. Phys. Chem. A*, 2003, **107**, 7619.
20 P. Hunt, D. R. Worrall, F. Wilkinson and S. N. Batchelor, *Photochem. PhotoBiol. Sci.*, 2003, **2**, 518.
21 J. Oakes, *Rev. Prog. Color.*, 2003, **33**, 72.
22 H. A. Schwarz, *J. Phys. Chem.*, 1989, **93**, 409.
23 P. Hunt, D. R. Worrall, F. Wilkinson and S. N. Batchelor, *J. Am. Chem. Soc.*, 2002, **124**, 8532.
24 P. Neta, J. Grodkowski and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1996, **25**, 709.
25 P. Yadav, P. O'Neill, S.N. Batchelor and B.S.M. Rao, *in preparation*.
26 S. N. Batchelor and H. Fischer, *J. Phys. Chem.*, 1996, **100**, 556.
27 A. Eli-Agamey and D. J. McGarvey, *Phys. Chem Chem. Phys.*, 2002, **4**, 1611.
28 M. Hoshino, R. Konishi, H. Seto, H. Sek, H. Sonoki, T. Yokoyama and H. Shimamori, *Res. Chem. Intermed.*, 2001, **27**, 189.
29 L. S. Scott, W.-J. Chen, A. Bakac and J. H. Epenson, *J. Phys. Chem.*, 1993, **97**, 6710.
30 S. Canonica, B. Hellrung and J. Wirz, *J. Phys. Chem A*, 2000, **104**, 1226.
31 R. A. Marcus, *Angew. Chem. Int. Ed Engl.*, 1993, **32**, 1111.
32 J. Oakes, *Rev. Prog. Color.*, 3002, **32**, 63.
33 S. E. Laursen, J. Hansen, T. A. Andersen and H. H. Knudsen, Danish EPA Working Report no. 10, 2002.
34 From the results in Fig. 1 and 2, approximately 2 ppm ketone is required to bleach 1 ppm of pure dye. Therefore for a strongly coloured effluent containing 10 ppm dye, 20 g of ketone costing ~0.3$ is required. If a lamp is used for photolysis an additional cost of ~0.3$ should be added and also the cost of a biological degradation step (~0.2$) following photolysis to remove the photoproducts of the ketone and hopefully also many of the photoproducts of the dye. This gives a total estimated cost of 0.8$/$m^3$ and may be compared to cost of 1$/$m^3$ or more for other methods, ref. 33.