

# Mechanistic study of the TiO<sub>2</sub>-assisted photodegradation of squarylium cyanine dye in methanolic suspensions exposed to visible light

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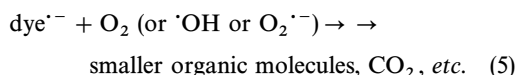
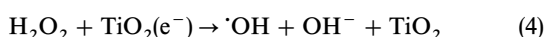
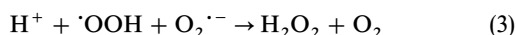
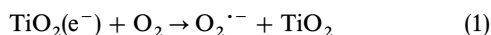
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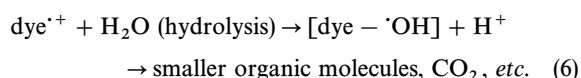
Details of the degradation pathway(s) of squarylium cyanine (SQ) dye in methanolic TiO<sub>2</sub> dispersions under visible light irradiation were probed in an attempt to more clearly understand the photodegradation mechanism of dye under visible radiation. For SQ, degradation begins by cleavage of the C=C double bond to yield ultimately the final product 1-sulfopropyl-3,3-dimethyl-5-bromoindolenium-2-one. A considerable amount of H<sub>2</sub>O<sub>2</sub> is also formed during degradation through reduction (but not through dismutation) of the superoxide radical anion. In comparison with the previous results in aqueous media, it is evidenced for the first time that the pathway for the TiO<sub>2</sub>-assisted photodegradation of SQ using visible light irradiation is initiated by a series of complex reactions involving the dye cation radical SQ<sup>•+</sup> with dissolved dioxygen and does not implicate any of the photogenerated active oxygen species such as <sup>•</sup>OH, O<sub>2</sub><sup>•-</sup> and <sup>•</sup>OOH radicals. These results clarify the previous equivocal conceptions on the details of the reaction between dye cationic radical and oxygen species.

In recent studies<sup>1–8</sup> we have shown that dyes can be photo-degraded in aqueous TiO<sub>2</sub> dispersions illuminated with visible light radiation. Others have reported similar studies.<sup>9–12</sup> Degradation by visible light in the presence of TiO<sub>2</sub> particles is a more practical and attractive method than the use of UV light to treat or pretreat dye pollutants in environmental waste waters because a larger fraction of the solar spectrum can be exploited in the visible wavelengths. Under visible irradiation, it is thought that the dye is excited (TiO<sub>2</sub> is not excited) by visible light to yield an excited state of the dye\*, which subsequently injects an electron into the conduction band of the semiconductor TiO<sub>2</sub>,<sup>7,8,13</sup> following which ensues a sequence of degradation events summarized in reactions (1) through (5):



Visible light radiation, air (dioxygen) and a semiconductor mediator such as TiO<sub>2</sub> are indispensable prerequisites<sup>3,5,9</sup> for the degradation process. Additionally, the appearance of ESR signals of DMPO–O<sub>2</sub><sup>•-</sup> and DMPO–<sup>•</sup>OH adducts<sup>4,6</sup> attests to the generation of hydroxyl and superoxide radical anions during the degradation. A considerable amount of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as another pivotal intermediate was also observed;<sup>8</sup> it was inferred that the electrons injected from the

excited dyes into TiO<sub>2</sub> are stored terminally in the form of hydrogen peroxide and dye degradation may not necessarily involve active oxygen species such as <sup>•</sup>OH, O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub>, at least in the systems examined.<sup>6,7</sup> With respect to eqn. (5), however, studies that address the real degradation steps and that probe which oxygen-containing species actually participate in the degradation (O<sub>2</sub>, <sup>•</sup>OH, O<sub>2</sub><sup>•-</sup> or all of these) have been relatively scarce.<sup>7</sup> Hydrolysis or solvolysis of dye radical cations formed<sup>12,14</sup> after injection of electrons may also lead to degradation.



To gain a better understanding of the visible irradiation pathway and to clarify some of the details of the degradation of squarylium cyanine dye in TiO<sub>2</sub> dispersions irradiated by visible light, we have extended the previous study carried out in aqueous media<sup>7</sup> to methanolic TiO<sub>2</sub> dispersions. Important intermediates and further details on the degradation pathway(s) are surveyed by UV-vis spectral changes, <sup>1</sup>H-NMR spectral changes, spin-trap EPR methods and by peroxide assays. Results strongly suggest that the TiO<sub>2</sub>-assisted photodegradation proceeds predominantly by direct oxygenation of the dye radical cations, dye<sup>•+</sup>. In addition, the successful degradation of dyes in methanolic TiO<sub>2</sub> dispersions may provide a practical direct treatment of dye pollutants in organic solvents.

## Experimental

### Photoreactor and light source

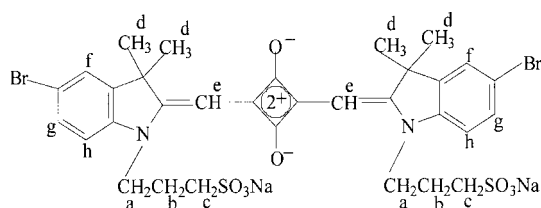
The visible light source was a 500 W halogen lamp positioned inside a cylindrical Pyrex vessel surrounded by a circulating

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water jacket (Pyrex) to cool the lamp. A cutoff filter was placed outside the Pyrex jacket to completely remove radiation below 420 nm and to ensure irradiation of the suspensions by visible light wavelengths only.

## Materials

TiO<sub>2</sub> powders used as the mediators (Degussa, P25, *ca.* 80% anatase, 20% rutile; BET area *ca.* 50 m<sup>2</sup> g<sup>-1</sup>) were kindly supplied by Degussa Co. The spin-trap reagents 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and  $\alpha$ -phenyl-*N*-tert-butyl-nitron (PBN) employed in the detection of active oxygen or carbon radicals were purchased from Sigma Chemical Co. Squarylium cyanine (in the structure the atom labels refer to the proton NMR analysis) was synthesized according to the method of Lin and Peng.<sup>15</sup> Horseradish peroxidase (POD) was obtained from Huamei Biologic Engineering Co. (China), superoxide dismutase (SOD) from the Research & Development Center of Biochemical Co. (Hebei, China), and *N,N*-diethyl-*p*-phenylenediamine (DPD) reagent from Merck (*p.a.*). Other chemicals were of analytical reagent grade quality and were used without further treatment.



Squarylium cyanine

## Procedures and analyses

Solutions of SQ at the desired concentrations were made up in water-free methanol as the solvent to which were added various amounts of TiO<sub>2</sub>. The resulting suspension was permitted to stand for *ca.* 30 min under vigorous stirring and aerated conditions in order to achieve an adsorption/desorption equilibrium between SQ and TiO<sub>2</sub> particles in the dark. Subsequently, the suspensions were subjected to various irradiation experiments. To assay intermediate changes, 4 mL samples of the suspensions were collected at given time intervals and were centrifuged to remove the TiO<sub>2</sub> particulates. The concentration of SQ in the centrifuged supernatant liquid was analyzed with a Lambda Bio20 UV-vis spectrophotometer (Perkin Elmer Co.). The concentration of H<sub>2</sub>O<sub>2</sub> in the supernatant liquid obtained by centrifugation and formed during irradiation of SQ-TiO<sub>2</sub> dispersions was examined by a photometric method.<sup>16</sup> The H<sub>2</sub>O<sub>2</sub> formed could not be detected directly because methanol inactivates the peroxidase. Consequently, the supernatant liquid was diluted one-fold with deionized and doubly distilled water and the resulting mixture containing H<sub>2</sub>O<sub>2</sub> was measured colorimetrically by means of a calibration curve obtained using otherwise identical procedures. Numerous runs showed that the modified procedure is applicable for assaying peroxides in the present methanol system. To probe the amount of H<sub>2</sub>O<sub>2</sub> adsorbed on the TiO<sub>2</sub> surface during SQ degradation, the TiO<sub>2</sub> samples were collected by centrifugation after complete discoloration of the dispersion; they were then dispersed in 7 mL of H<sub>2</sub>O followed by addition of a color-developing reagent (DPD or POD) and by further removal of TiO<sub>2</sub>. The colored solution containing H<sub>2</sub>O<sub>2</sub> was assayed by UV-vis spectroscopy.

Proton NMR spectra were obtained with a Varian 300 nuclear magnetic resonance spectrometer. The samples for <sup>1</sup>H-NMR examination were prepared as follows: several individual dispersions containing 20 mL of 8.3 × 10<sup>-4</sup> M SQ dye and 50 mg TiO<sub>2</sub> were irradiated at different time intervals;

then the TiO<sub>2</sub> particles were removed by centrifugation. The supernatant liquid was distilled under reduced pressure to remove methanol. The remaining residue was subsequently dissolved in 0.5 mL DMSO-*d*<sub>6</sub> for NMR determination.

Electron paramagnetic resonance (EPR) signals of paramagnetic species spin trapped with DMPO or PBN were recorded with a Bruker EPR 300E spectrometer to ascertain the formation of active radical species during irradiation of the dye-TiO<sub>2</sub> dispersions. The irradiation source ( $\lambda$  = 532 nm) was a Quanta Ray Nd : YAG pulsed (10 Hz) laser system. The settings for the EPR spectrometer were: center field = 3486.70 G; sweep width = 100.0 G; microwave frequency = 9.82 GHz; power = 5.05 mW.

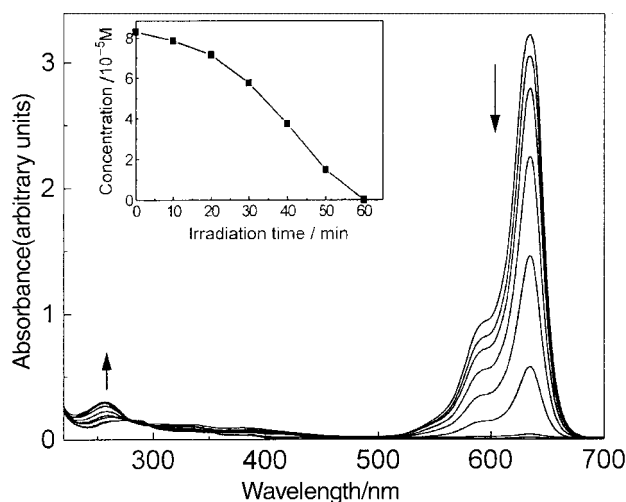
## Results and discussion

### UV-vis spectral assays

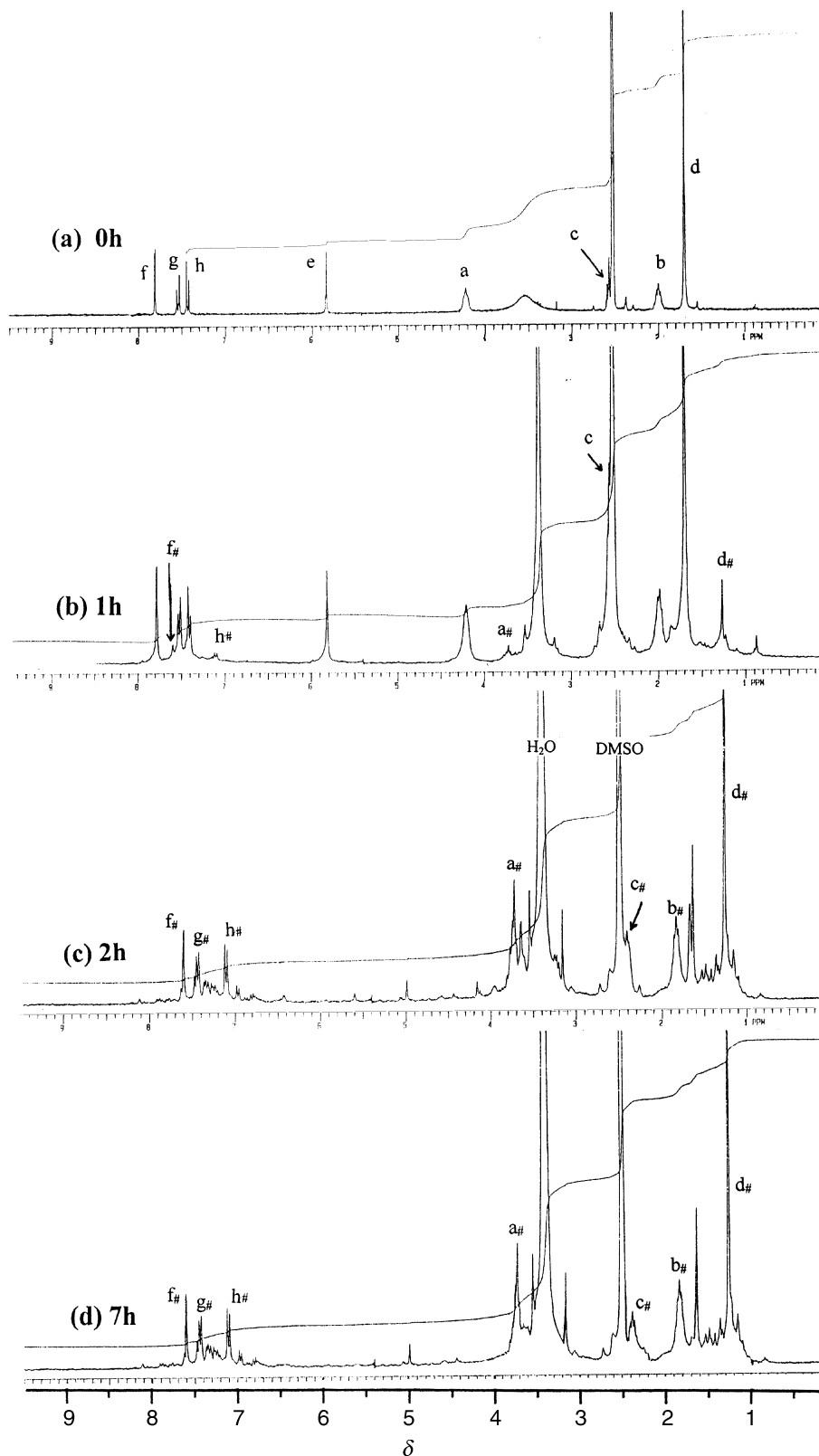
Control experiments showed that the dye SQ is stable and is not degraded in visible-light-irradiated TiO<sub>2</sub> dispersions purged with nitrogen or in aerated solutions illuminated with visible light in the absence of TiO<sub>2</sub> particles. However, rapid disappearance of SQ occurred when air-equilibrated SQ-TiO<sub>2</sub> suspensions were exposed to visible light (Fig. 1). They exhibited rather characteristic degradation kinetics (inset to Fig. 1) with an initially short induction period (*ca.* 20 min) followed by pseudo-zero-order kinetics upon further irradiation to 60 min. Only *ca.* 2% of SQ is adsorbed in the dark on the TiO<sub>2</sub> surface in methanolic dispersions, much less than in aqueous media (39% adsorption) under otherwise identical conditions.<sup>7</sup>

### <sup>1</sup>H-NMR spectral assays

<sup>1</sup>H-NMR spectral changes were recorded for several individually irradiated 20 mL dispersions using procedures indicated in the Experimental section. The results are displayed in Fig. 2. An increase in irradiation time led to a gradual disappearance of the H<sub>e</sub> signal ( $\delta$  5.85) on the C=C double bond; concomitantly, the signals of the other protons shifted to higher field. These are the same features as reported earlier<sup>7</sup> in aqueous TiO<sub>2</sub> dispersions; the photodegradation of SQ occurs by cleavage of the C=C bond in both aqueous and methanolic TiO<sub>2</sub> dispersions. The main residual fragment was confirmed, by methods similar to those used earlier,<sup>7</sup> to be a 1-



**Fig. 1** Spectral changes of SQ in methanolic TiO<sub>2</sub> dispersions under visible light irradiation (halogen lamp) for different times (10 min intervals). Initial [SQ] = 8.3 × 10<sup>-5</sup> M; TiO<sub>2</sub> loading, 20 mg in 50 mL. Inset: concentration (determine by absorbance) change *vs.* irradiation time. All spectra were obtained after the removal of TiO<sub>2</sub> particles and 5-fold dilution with water.



**Fig. 2**  $^1\text{H}$ -NMR spectra after various irradiation times (halogen lamp) during the photodegradation of SQ dye (for details, see text).

sulfopropyl-3,3-dimethyl-5-bromoindolenium-2-one species. This intermediate product is not degraded upon further irradiation (see spectra *c* and *d* in Fig. 2) because it does not absorb visible light. The similar trends in NMR spectral changes in aqueous and methanolic suspensions infer that on illumination dye decomposition occurs through reaction of dissolved dioxygen (rather than with photogenerated  $\text{H}_2\text{O}_2$  or  $\text{O}_2^{\cdot-}$ , see below) with the dye $^{\cdot+}$  cation radicals. These results preclude the hydrolysis or solvolysis of dye cationic radicals as the mechanism in so far as the NMR spectral changes should

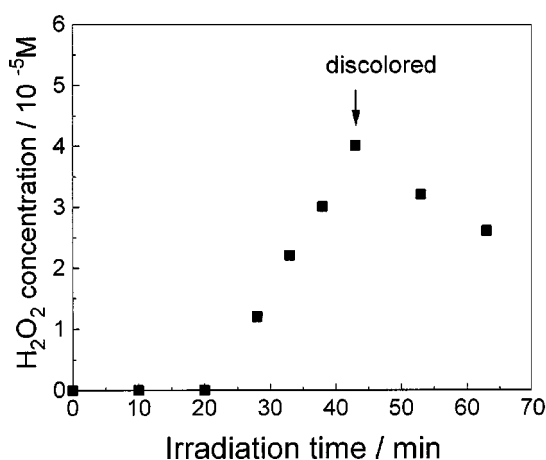
have displayed different features if hydrolysis in aqueous media or solvolysis in methanol were the operating pathways.

#### Peroxide measurements

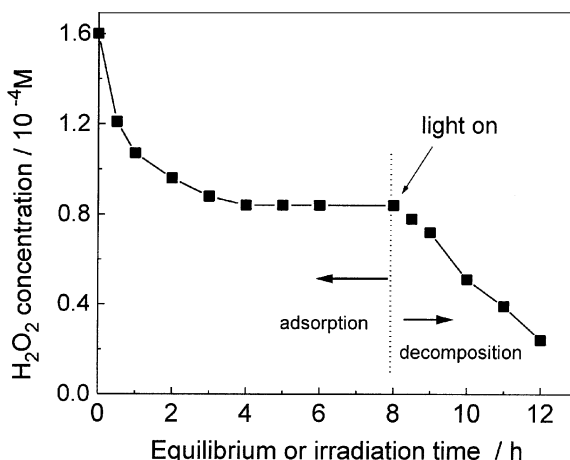
Formation of peroxides during the SQ dye degradation was examined by the horseradish peroxidase method. Surprisingly, peroxide was observed in visible irradiated SQ-TiO<sub>2</sub> methanolic dispersions, and tested to be  $\text{H}_2\text{O}_2$  rather than organoperoxides as documented previously.<sup>7,8</sup> At first, when

50 ml of a  $8.3 \times 10^{-5}$  M SQ methanolic solution was irradiated by visible light in the presence of 20 mg of  $\text{TiO}_2$  particles, no  $\text{H}_2\text{O}_2$  was detected in the bulk solution. However, a considerable amount of  $\text{H}_2\text{O}_2$  was detected adsorbed on the surface of the  $\text{TiO}_2$  particles ( $1.6 \times 10^{-7}$  moles, corresponding to *ca.*  $9.6 \times 10^{-2}$  molecule  $\text{nm}^{-2}$ ) when assaying the  $\text{TiO}_2$  particulates according to the procedure described in the Experimental section, following complete discoloration of the dispersion. To facilitate formation of  $\text{H}_2\text{O}_2$  and thus detection, a greater concentration of SQ dye ( $2.7 \times 10^{-4}$  M) was employed to increase the concentration of  $\text{H}_2\text{O}_2$  generated in the bulk solution. After a brief induction period (about 20 min), the concentration of generated  $\text{H}_2\text{O}_2$  detected in the bulk first increased with irradiation time but then decreased after complete discoloration of SQ (Fig. 3). The fact that no  $\text{H}_2\text{O}_2$  was detected during the first 20 min and that the observed  $\text{H}_2\text{O}_2$  concentration diminished after complete discoloration of SQ is attributed to adsorption of generated  $\text{H}_2\text{O}_2$  on the  $\text{TiO}_2$  particulates followed by its photoinduced decomposition by visible light illumination. Accordingly, it was necessary to verify the extent of  $\text{H}_2\text{O}_2$  adsorption and its photodecomposition on the surface of  $\text{TiO}_2$  particles in methanolic dispersions.

As illustrated in Fig. 4,  $\text{H}_2\text{O}_2$  is adsorbed to a great extent on  $\text{TiO}_2$  particles. On irradiation with visible light it photodecomposes. Interaction of hydrogen peroxide with the  $\text{Ti(IV)}$  ions on the  $\text{TiO}_2$  particle surface<sup>17–23</sup> yields yellow surface



**Fig. 3** Transient concentration of  $\text{H}_2\text{O}_2$  formed in methanolic  $\text{TiO}_2$  dispersions (7.5 mL) containing SQ dye under visible light irradiation (halogen lamp). Initial  $[\text{SQ}] = 2.7 \times 10^{-4}$  M;  $\text{TiO}_2$  loading, 20 mg per 7.5 mL (for detailed procedure, see Experimental section).



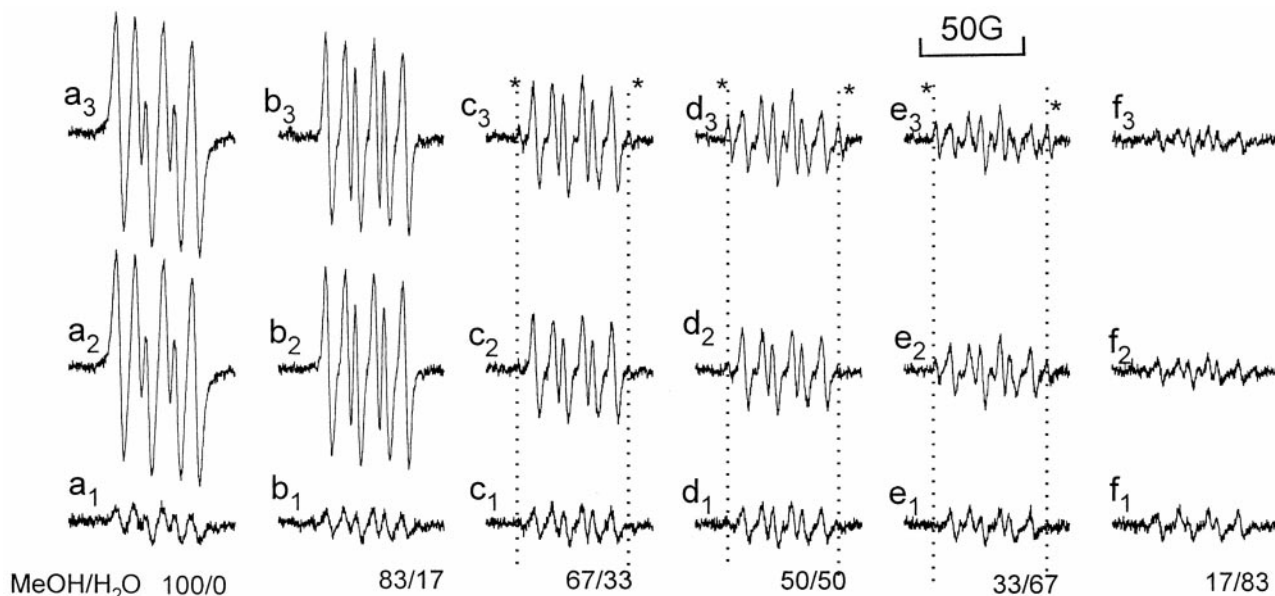
**Fig. 4** Concentration changes of adsorbed  $\text{H}_2\text{O}_2$  with equilibrium time in the dark followed by photodecomposition *vs.* irradiation time in methanolic dispersions. Initial  $[\text{H}_2\text{O}_2] = 1.6 \times 10^{-4}$  M;  $\text{TiO}_2$  loading, 20 mg per 50 mL.

complexes capable of photodecomposing when exposed to visible light.<sup>8</sup> Consequently, based on the adsorption and photodecomposition of  $\text{H}_2\text{O}_2$  the real concentration of  $\text{H}_2\text{O}_2$  produced is greater than the observed maximum quantity,  $4.0 \times 10^{-5}$  M (Fig. 3), inferring that the electrons injected from the excited dyes are primarily stored in the form of  $\text{H}_2\text{O}_2$  *via* 2-electron reduction of dioxygen adsorbed on  $\text{TiO}_2$  (see also EPR results below). In fact, the active oxygen species,  $\text{O}_2^{\cdot-}$  and/or  $\cdot\text{OOH}$  radicals, have a low steady-state concentration due to fast reduction into  $\text{H}_2\text{O}_2$  in methanolic dispersions or else reaction at a high rate with the cation radical. However, since a high concentration of  $\text{H}_2\text{O}_2$  is formed (from the reduction of superoxide radicals, see below) and addition of spin-trap PBN did not inhibit the degradation of the dye, we deduce that  $\text{O}_2^{\cdot-}$  and/or  $\cdot\text{OOH}$  radicals are mainly reduced to form  $\text{H}_2\text{O}_2$  and are minor components that contribute negligibly to dye degradation, although these species were observed by spin-trap EPR techniques (very weak signals, see below).

### EPR spectral assays

EPR spectral variations in SQ- $\text{TiO}_2$  dispersions that were irradiated for 2 min with laser radiation in a 10 ml Pyrex vessel and then diluted with  $\text{H}_2\text{O}$  were recorded in a quartz capillary; they are illustrated in spectra  $a_1, b_1, c_1, d_1, e_1$  and  $f_1$  of Fig. 5. These EPR spectra are the typical signatures of  $\text{DMPO-O}_2^{\cdot-}$  adducts; no new other signals appeared that might have originated from species such as  $\text{DMPO}\cdot\text{OH}$  and  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  adducts subsequent to an increase in the  $\text{H}_2\text{O}$  content in methanol-water mixtures. This shows that disproportionation or dissociation of  $\text{DMPO-O}_2^{\cdot-}$  adducts does not occur, even in solvent mixtures containing 83%  $\text{H}_2\text{O}$  (see spectra  $f_1$ ) in contrast to the reports that  $\text{DMPO-O}_2^{\cdot-}$  adducts transform rapidly into  $\text{DMPO}\cdot\text{OH}$  adducts.<sup>24</sup> However, when the samples displaying spectra  $a_1-f_1$  were subjected *in situ* to laser irradiation for 1 and 2 min, new signals appeared with different intensities in spectra  $c_2, c_3, d_2, d_3$  and  $e_2, e_3$  and the patterns became more complicated, especially in spectra  $d_2, d_3, e_2, e_3$ ; no new relevant signals appeared in spectra  $a_2, a_3, b_2, b_3$  and  $f_2, f_3$ . In spectra  $c-e$ , the new signals for the different samples are located at the same magnetic field positions (noted with an asterisk).

Compared with the typical  $\cdot\text{OH}$ ,  $\cdot\text{CH}_2\text{OH}$  and  $\text{O}_2^{\cdot-}$  radical adducts obtained under analogous conditions (Fig. 6), these new signals such as in spectra  $d_3$  in Fig. 5 can be assigned to the  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  adducts originating from the attack of generated  $\cdot\text{OH}$  radicals on methanol molecules in the  $\text{CH}_3\text{OH-H}_2\text{O}$  solvent mixture.<sup>7</sup> This result also demonstrates that  $\text{CH}_3\text{OH}$  is an effective  $\cdot\text{OH}$  scavenger, which competes even with the spin-trap DMPO under the present experimental conditions. In spectra  $a_2, a_3$  and  $b_2, b_3$ , a drastic increase in intensity of the  $\text{DMPO-O}_2^{\cdot-}$  signals is noticeable from  $a_1$  to  $a_3$  and from  $b_1$  to  $b_3$  (Fig. 5) during laser irradiation, which clearly indicates that only  $\text{O}_2^{\cdot-}$  radicals were produced whereas the  $\cdot\text{OH}$  and  $\cdot\text{CH}_2\text{OH}$  radicals were totally absent in  $\text{MeOH-H}_2\text{O}$  dispersions containing less than 17%  $\text{H}_2\text{O}$  and irradiated with visible light. The spectral changes from  $f_1$  to  $f_3$  were also expected to display evidence for  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  adducts in addition to  $\text{DMPO-O}_2^{\cdot-}$  according to the overall change tendencies (spectra  $c, d, e$ ). We failed to observe these signals because the quantities of dye and  $\text{TiO}_2$  in the irradiated SQ- $\text{TiO}_2$ - $\text{CH}_3\text{OH-H}_2\text{O}$  system were too small when the original dispersion content was only 17%. Additionally, the EPR signals of  $\text{DMPO-O}_2^{\cdot-}$  adducts were observed when the methanolic dispersions ( $[\text{SQ}] = 8.3 \times 10^{-4}$  M, 0.5 mL;  $\text{TiO}_2$ , 5 mg) were exposed to visible radiation from a halogen lamp until total discoloration of SQ and after addition of the spin-trap DMPO. Further examination revealed that the intensities of the EPR signals were nearly equal both in the

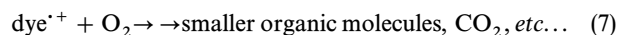


**Fig. 5** EPR spectral changes of  $8.3 \times 10^{-4}$  M SQ methanolic dispersions (5 mL) in a Pyrex vessel containing 20 mg  $\text{TiO}_2$  and 30 mg DMPO (0.053 M) after 2 min irradiation by monochromatic laser light ( $\lambda = 532$  nm). The dispersion was subsequently diluted with  $\text{H}_2\text{O}$  to the indicated ratios of irradiated methanolic dispersions- $\text{H}_2\text{O}$ : 100 : 0, 83 : 17, 67 : 33, 50 : 50, 33 : 67, 17 : 83, for a to f, respectively. Changes were measured in a quartz capillary in the EPR cavity (see spectra  $a_1$ - $f_1$ ). Spectra  $a_2$ - $f_2$  were recorded after further laser irradiation *in situ* for 1 min of samples  $a_1$ - $f_1$ . Spectra  $a_3$ - $f_3$  correspond to a further 1 min *in situ* irradiation with laser light.

spectra of the dispersions and of the bulk solution after the removal of  $\text{TiO}_2$  particles. This demonstrates that there is no significant adsorption of  $\text{O}_2^{\cdot-}$  or of the  $\cdot\text{OOH}$  species on the  $\text{TiO}_2$  particle surface in spite of the large  $\text{TiO}_2$  loading, 5 mg per 0.5 mL solution. This evidence is consistent with the notion that a considerable amount of the  $\text{H}_2\text{O}_2$  detected must originate from further reduction of  $\text{O}_2^{\cdot-}$  or  $\cdot\text{OOH}$  in methanolic dispersions during the degradation process, rather than from the disproportionation of  $\text{O}_2^{\cdot-}$  or  $\cdot\text{OOH}$  during measurements when  $\text{H}_2\text{O}$  is added to the bulk methanol solution. If only the  $\text{O}_2^{\cdot-}$  (or  $\cdot\text{OOH}$ ) species, but not  $\text{H}_2\text{O}_2$ , were present in the methanolic  $\text{TiO}_2$  dispersion, there would be no detectable  $\text{H}_2\text{O}_2$  when analyzing the  $\text{TiO}_2$  particulates removed from the discolored dye- $\text{TiO}_2$  dispersion because of negligible adsorption of the superoxide radical anion species. In addition, the weak DMPO- $\text{O}_2^{\cdot-}$  signals imply that the concentration of  $\text{O}_2^{\cdot-}$  species present in this system is rela-

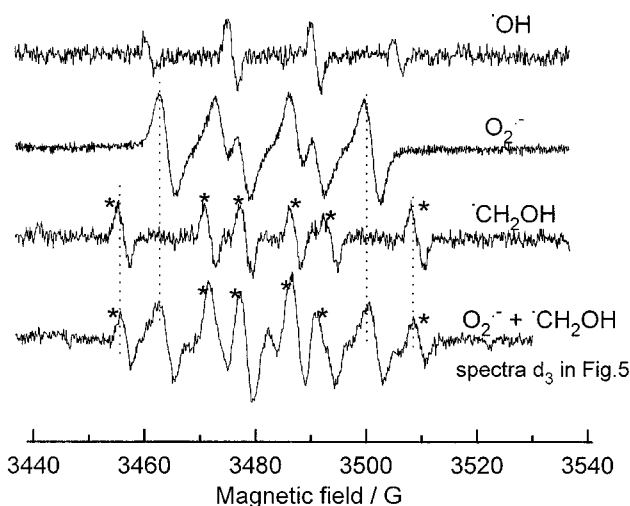
tively small and most of these species are converted to  $\text{H}_2\text{O}_2$ . It should be noted that all the EPR signals in Fig. 5 were obtained when the spin-trap reagent DMPO was added to the dispersions before laser irradiation, whereas all the signals discussed here were determined after addition of the DMPO spin-trap to the dispersions that contained dyes totally discolored by irradiation from the halogen lamp source. From these findings, it is clear that  $\cdot\text{OH}$  radicals are not produced during degradation of pure methanolic dispersions or even when the methanolic dispersions contained 17%  $\text{H}_2\text{O}$  (see spectra  $a_1$  to  $a_3$  and  $b_1$  to  $b_3$ ).

PBN is another excellent spin-trap reagent for superoxide radicals, which displays a characteristic three-group double peak signal representative of PBN- $\cdot\text{OOH}$  species. When the dispersion was irradiated by visible laser light, the typical EPR signals of PBN- $\cdot\text{OOH}$  appeared (spectra are not shown), indicating that superoxide radicals are present in the dispersion systems. In the present study, PBN was also used as an additive to the methanolic SQ- $\text{TiO}_2$  dispersions illuminated by visible light from the halogen lamp in order to efficiently scavenge active oxygen species and to observe whether the degradation still proceeded after the superoxide radicals were trapped. Comparison with the case in which the spin-trap PBN is absent, addition of the spin trap at greater concentrations did not retard the degradation of SQ. This result highlights the notion that dye degradation is independent of the presence of superoxide radical species and that the only possibility for dye degradation to occur is through reaction of the dye cation radicals with dissolved dioxygen [eqn. (7)]:



## Conclusions

Degradation of the dye SQ is initiated by photoinduced cleavage of the C=C double bond in methanolic  $\text{TiO}_2$  dispersions irradiated by visible light; a remarkable amount of  $\text{H}_2\text{O}_2$  is produced in the degradation processes. The  $\text{O}_2^{\cdot-}$  or  $\cdot\text{OOH}$  radicals are present only at relatively low concentrations in methanolic dispersions and are converted rapidly to  $\text{H}_2\text{O}_2$  by a reductive process involving the electron from the excited dyes injected onto the  $\text{TiO}_2$  particles. Changes in the  $^1\text{H}$ -NMR profile in methanolic media are similar to those



**Fig. 6** EPR spectra of radical adducts with DMPO in SQ- $\text{TiO}_2$  dispersions: (a) DMPO- $\cdot\text{OH}$  formed in irradiated aqueous dispersions; (b) DMPO- $\text{O}_2^{\cdot-}$  in irradiated methanol dispersions; (c) DMPO- $\cdot\text{CH}_2\text{OH}$  in irradiated methanol-water dispersions ( $[\text{SQ}] = 8.3 \times 10^{-4}$  M, for additional details see ref. 7); (d) spectrum  $d_3$  of Fig. 5.

observed in *aqueous* media. Together with the fact that the degradation is not hindered by addition of PBN, a scavenger of superoxide radicals, the results strongly suggest that the degradation of SQ occurs through reaction of  $\text{dye}^{\cdot+}$  cation radicals with dissolved dioxygen, rather than with the photo-generated active oxygen species or with the solvents (hydrolysis or methanolysis).

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