EPR study of spin-trapped free radical intermediates formed in the heterogeneously-assisted photodecomposition of acetaldehyde †

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Electron paramagnetic resonance spectroscopy is used to detect radical adducts of PBN (α-phenyl *N-tert*-butyl nitrone) generated by exposure of solutions and suspensions to ambient or high power UV at 300 K. Exposure of acetaldehyde to direct sunlight generates a different PBN radical adduct to high power UV irradiation. Direct sunlight irradiation of deoxygenated acetaldehyde generates PBN–acetyl adducts whereas direct sunlight exposure of oxygenated acetaldehyde produces PBN–acetoxyl adducts. High power UV irradiation of TiO_2/acetaldehyde suspensions yields the same radical adduct generated when no TiO_2 is present—this adduct (assigned to trapped formyl radicals or PBN degradation products) is produced irrespective of the state of oxygenation of solution. Direct sunlight irradiation of deoxygenated TiO_2/acetaldehyde suspension results in the production of PBN–acetyl adducts as the primary species. In oxygenated TiO_2/acetaldehyde suspension, PBN–acetyl adducts are again produced as the primary species, together with a weakly adducted secondary species—assigned to PBN–acetoxyl adducts. TiO_2 band gap transitions are observed to play no part in the production of radical intermediates in sunlight irradiated acetaldehyde/TiO_2 suspension. The extent of non-band gap dependent processes is shown to be sensitive to the surface basicity of the metal oxide. Band gap mediated radical production is demonstrated to arise when acetaldehyde photoreduction is coupled to the concomitant photooxidation of ethanol. Ethanol derived PBN–ethoxy adducts are detected as the primary species arising from sunlight irradiation of both oxygenated and deoxygenated TiO_2/acetaldehyde/ethanol suspensions.

1. Introduction

Over the period since 1971, when Fujishima and Honda[1] first reported the use of TiO_2 in splitting water for solar energy conversion, the use of irradiated semiconductor suspensions for the purpose of photomineralization of organic pollutants has received continual and growing scientific interest. Chlorinated hydrocarbons were the earliest pollutant substrates to be studied in heterogeneous photocatalytic systems,[2] most probably because of their high toxicity and common occurrence as industrial effluents, and many detailed mechanisms for their photocatalytic destruction have been reported.[3] Although there have now been many studies conducted for a wide range of organic contaminants—from simple alkanes to pesticides and dyes[4]—there have been relatively few studies conducted concerning the detailed photodegradative mechanism for aliphatic aldehydes.

Sources of aldehyde pollution range from their use in industry as synthetic precursors, where effluent discharges may cause soil and groundwater contamination, to atmospheric emissions arising from vehicle exhausts (ppm range) and slow release from synthetic furnishing materials (sub-ppm range). In photochemical smogs they are readily converted into respiratory irritants such as peroxyacyl nitrate and the possible mutagenic effects of long term, low level indoor exposure are still largely unknown.[5] It is the destruction of such airborne organic pollutants that perhaps still poses one of the biggest challenges for environmental scientists.

The recent interest in photocatalytic decontamination systems is driven by the search for clean effluent disposal technologies. The photo-mineralization reaction (1) has the advantage

$$\text{Organic substrate} + O_2 \xrightarrow{\text{photocatalyst}} CO_2 + H_2O \quad (1)$$

over many other clean-up technologies of producing relatively non toxic waste materials, even though the treated effluent cannot be considered as totally innocuous within the living environment.

The TiO_2 catalysed photomineralization of organic species is a complex process which has been shown, in many cases, to involve surface bound hydroxyl radical intermediates.[6] However, the mechanism of aldehyde photoreaction at TiO_2 surfaces is known to proceed *via* a non-conventional route.[7]

In this study, spin trapping is used to detect radical intermediates formed during the room temperature photoreaction of acetaldehyde in a TiO_2 suspension. The spin trapping technique affords the indirect detection of short-lived radicals which, when present at low steady state concentrations, cannot be detected easily by other spectroscopic methods. The spin trap α-phenyl *N-tert*-butyl nitrone (PBN) has been employed successfully to detect radical intermediates in the similar phenol/TiO_2 photoredox system.[8] The coupling of acetaldehyde photoreduction to the concomitant photooxidation of ethanol is observed to result in a large increase in the number of radical intermediates trapped. We also report that the initial photoexcitation of substrate—as opposed to the classical mechanism of initial excitation of semiconductor—may result in an enhancement of the rate of photoredox processes, particularly at high photon fluxes.

2. Experimental

2.1 Chemicals

Rutile titanium dioxide and $AlPO_4$-coated TiO_2 were supplied by Tioxide UK Ltd. (surface areas 93 and 7.7 $m^2\ g^{-1}$, respectively). MgO was supplied by Johnson Matthey (surface area ≈150 $m^2\ g^{-1}$). Surface area measurements were made by single point N_2 adsorption. The spin trapping reagent α-phenyl *N-tert*-butyl nitrone (PBN) was supplied by Aldrich Chemicals, and stored at 273 K in the dark. Acetaldehyde and ethanol (supplied by Aldrich Chemicals) were analytically pure, and

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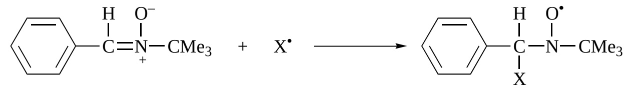
stored at 295 K in the dark. All powders were pre-treated by heating to 600 K at 10^{-4} mbar for 2 h to remove surface carbon impurities.

2.2 Experimental procedures

The spin trap concentration was 0.05 mol dm^{-3} in all experiments. The mode of action of the spin trap is shown in Scheme 1. The extent of the hyperfine interactions between the unpaired electron and the nitrogen and α-hydrogen nuclei are dependent upon both the nature of the radical adducted and the solvent employed. Deoxygenation of solutions was carried out by repeated freeze–pump–thaw cycles. Deoxygenated solutions were maintained under a nitrogen atmosphere. Oxygenation of solutions was carried out by bubbling air through the solution for 20 min at 293 K. Oxygenated solutions were maintained under an atmosphere of air. All oxygenation/deoxygenation procedures were performed in a quartz cell of 1 cm internal diameter, in the dark. In the case of all powder suspension studies, the powder : solution ratio was 0.01 g per gram. A 600 W high pressure Hg/Xe lamp, of broad band λ output (Oriel Instruments), fitted with a water filter, was used for high power irradiation of solutions. Ambient irradiations were carried out by standing solutions in direct unfocused sunlight, in quartz cells (1 cm inside diameter) which were sealed with rubber septa. EPR spectra were recorded at 293 K on a Varian E109 spectrometer operating at 100 kHz modulating frequency and connected to a Stellar DS/EPR data acquisition system.



Scheme 1 Mode of action of the spin trap PBN

3. Results and discussion

Titanium dioxide has been the most widely studied semiconductor photocatalyst for the destruction of organic wastes. It occurs naturally in three crystalline forms, anatase, rutile and brookite—the latter form having no practical use in photocatalytic systems. Anatase is the most active form, with a band gap energy equal to 3.2 eV compared to 3.0 eV for rutile.[9] Consequently, anatase absorbs electromagnetic radiation less than 380 nm whilst rutile absorbs wavelengths below 405 nm. Fig. 1 shows the main photoprocesses which occur during the TiO_2-sensitised heterogeneous photocatalytic mineralization of organics. The primary photochemical event is the absorption of a UV photon by the semiconductor, and this absorption excites an electron from the filled valence band to the conduction band [reaction (1)]. The negatively charged surface hydroxy groups, which terminate the TiO_2 lattice, cause upward bending of the electron bands. There is, therefore, a tendency for the electrons to be repelled and the positive holes to be attracted to the surface. Consequently, the electrons and holes tend to move apart and this reduces their recombination rate [reaction (2)]. Despite this, most of the excited electrons and valence band holes either recombine at recombination centres or are trapped at electron or hole traps [steps (5) and (6)]. At the surface, holes are trapped by hydroxy groups and form hydroxyl radicals which can participate in subsequent chemical reactions. Similarly, electrons can be trapped by adsorbed oxygen to form the adsorbed $O_2^{\cdot -}$. The excited electrons can reduce the oxidised forms of redox couples with a redox energy beneath that of the conduction band, and holes can similarly oxidise the reduced form of redox couples with a redox energy above the valence band. Both processes—reduction by e_{cb} and h_{vb}—may occur competitively when more than one type of reactant is available for adsorption. A general photoreaction sequence is given in Scheme 2.

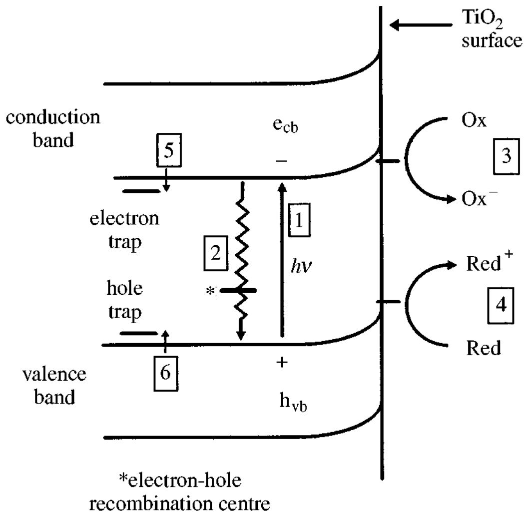


Fig. 1 Photoinduced charge-transfer processes in TiO_2 suspensions (CB = conduction band, VB = valence band). 1, Absorption of a UV photon to produce valence band holes (h_{vb}) and conduction band electrons (e_{cb}); 2, electron–hole recombination; 3, reduction of adsorbed substrate by e_{cb} at the conduction band edge; 4, oxidation of adsorbed substrate by h_{vb} at the valence band edge; 5, e_{cb} trapping at a lattice defect; 6, h_{vb} trapping at a lattice defect.

(*a*) Production and initial reaction of electron–hole pairs

$$TiO_2 + h\nu\ (\lambda < 400\ \text{nm}) \longrightarrow h_{vb} + e_{cb} \qquad (2)$$

$$h_{vb} + OH_{(ADS)} \longrightarrow OH\cdot \qquad (3)$$

$$e_{cb} + O_{2(ADS)} \longrightarrow O_2^{\cdot -} \qquad (4)$$

(*b*) Primary photodissociation events

$$CH_3CHO \longrightarrow CH_3\cdot + CHO\cdot\ (\lambda < 340\ \text{nm}) \qquad (5)$$

$$CH_3CHO \longrightarrow \cdot CH_2CHO + H\cdot\ (\lambda < 220\ \text{nm}) \qquad (6)$$

$$CH_3CHO \longrightarrow CH_3CO\cdot + H\cdot\ (\lambda < 310\ \text{nm}) \qquad (7)$$

(*c*) Oxidation of primary photolysis products

$$CH_3CO\cdot + O_2 \longrightarrow CH_3CO_3\cdot \qquad (8)$$

$$CH_3CO_3\cdot + CH_3CHO \longrightarrow CH_3CO_3H + CH_3CO\cdot \qquad (9)$$

$$CH_3CO_3H + CH_3CHO \longrightarrow 2\ CH_3CO_2H \qquad (10)$$

Scheme 2

The steady state concentration of surface electrons and holes is controlled by the electron–hole recombination in the bulk of the solid—a bimolecular reaction. Because of this, the surface concentration of electrons, or holes, varies not as the intensity of the UV radiation but as its square root.

Photocatalytic mineralization processes have been shown by many authors[11,12] to be oxidatively coupled to the trapping of valence band holes by surface hydroxyls—the trapping process occurring primarily at the most coordinatively saturated, and therefore most basic, OH groups.[13] Joyce-Pruden *et al.*[14] have shown that the addition of NaOH, in amounts not exceeding the number of TiO_2 surface sites available for OH adsorption, leads to a significant increase in the quantum efficiency of TiO_2 catalysed photo-processes. Surface bound OH· has been shown to be a 'transient species'[15] on TiO_2, and there is a wealth of EPR evidence available, using the spin trapping method, to demonstrate that OH· radicals participate in the photocatalytic oxidation of many organic molecules.[6] The spin adduct parameters for OH· trapped in irradiated colloidal TiO_2 systems were reported as long ago as 1979 by Bard.[16] Aliphatic compounds may react directly with photogenerated holes ($R + h_{vb} \longrightarrow R\cdot + H^+$), or with the photogenerated OH· radical (R + OH·

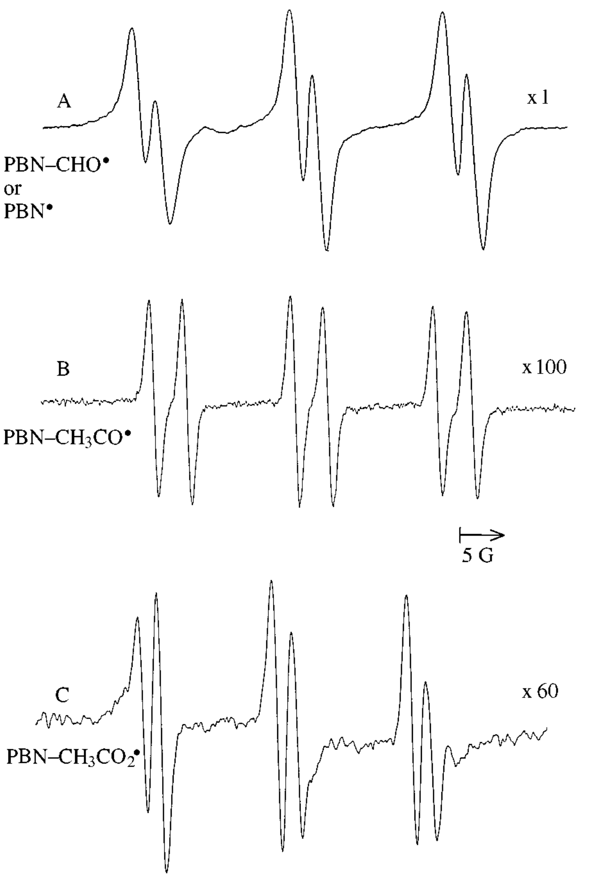


Fig. 2 EPR spectra of PBN spin adducts. (A) 600 W UV irradiation (6 s) of neat acetaldehyde; (B) 20 min direct sunlight irradiation of deoxygenated acetaldehyde; (C) 20 min direct sunlight irradiation of oxygenated acetaldehyde.

$\longrightarrow$ R· + H_2O).[6,16] Hydrogen abstraction by OH· is very fast[17] and either mechanism results in the production of the same aliphatic radical, which is then capable of reacting with O_2 to produce an organoperoxy radical, $RO_2\cdot$. The fates of photogenerated electrons have been recently investigated[7] and it has been shown that, in aerated suspensions, e_{cb} can be reductively coupled through reaction with adsorbed O_2 ($e_{cb} + O_{2(ADS)} \longrightarrow O_2^{\cdot -}$). The superoxide radical anion thus produced is postulated to further react to form peroxide ($O_2^{\cdot -} + H^+ \longrightarrow$ ·OOH) or to combine with an organoperoxy radical to yield an unstable tetraoxide intermediate ($RO_2\cdot + O_2^{\cdot -} \longrightarrow ROOOO^-$).[7] The bimolecular combination of two superoxide anion radicals is known to be very slow in comparison with the rate of combination of an organoperoxy species. Anpo *et al.*[18] have demonstrated clearly the formation of superoxide radicals on irradiated TiO_2 surfaces.

The aliphatic aldehydes are electron rich and have reduction potentials of −1.48 to −1.90 eV *vs.* SCE (standard calomel electrode) compared to −0.85 eV *vs.* SCE for the electron deficient aromatic aldehydes, *e.g.*, benzaldehyde.[19] In contrast to an electron deficient aldehyde, the reduction potential of an aliphatic aldehyde does not lie close to the conduction band edge of TiO_2. As a consequence of this, the photocatalytic reduction of aliphatic aldehydes occurs at a much slower rate—even when coupled to the oxidation of a highly efficient electron donor such as ethanol. Schwitzgebel *et al.*[7] have also shown that the photocatalytic air oxidation of aliphatic aldehydes does not follow the mechanistic scheme outlined above—Scheme 2 shows the main aldehyde photoprocesses. Due to the high reactivity of the H atom of the terminal carbonyl function, aliphatic aldehydes are efficient reducing agents. Thus, hydrogen abstraction by h_{vb} or $OH\cdot_{(SURF)}$ is readily accomplished, and serves as the initiation step in the photocatalytic air oxidation of aliphatic aldehydes. Following the initiation step, the process continues as a conventional alkylcarbonyl radical propagated chain reaction, in which neither conduction band electrons or $O_2^{\cdot -}$ participate.

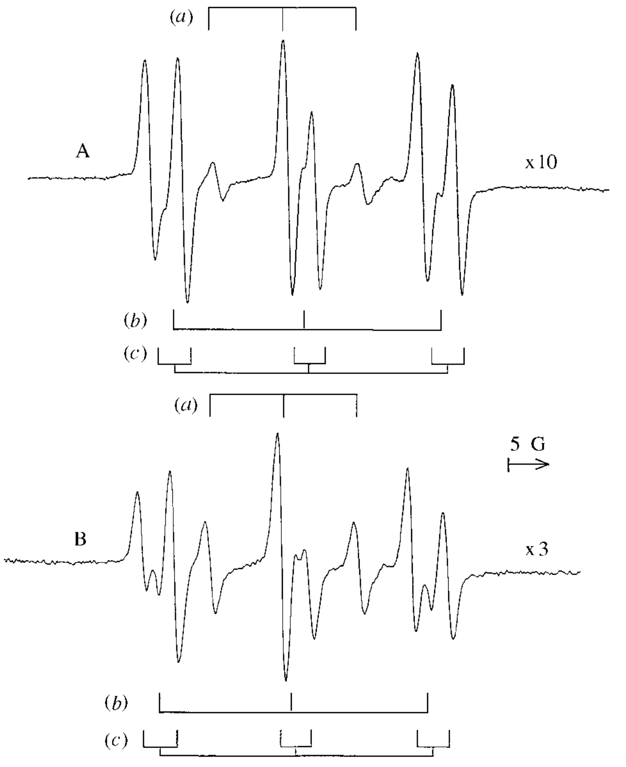


Fig. 3 EPR spectra of PBN spin adducts. (A) 20 min direct sunlight irradiation of TiO_2/acetaldehyde suspension (coated and uncoated TiO_2 produce the same adducts); (B) 20 min direct sunlight irradiation of MgO/acetaldehyde suspension.

Recent studies have shown that both photoreduction and photooxidation by TiO_2 can be effected in non aqueous media.[20] In the case of aliphatic aldehydes, the heterogeneous photocatalytic process has been observed to halt when the aldehyde becomes predominant in light absorption,[14] *i.e.*, there is a critical aldehyde concentration above which the semiconductor initiated photocatalysis is shut down due to the inefficient recycling of the photogenerated electron. We are able to show, however, that radical intermediate formation still occurs even when the critical aldehyde concentration is exceeded.

3.1 Radicals generated in the absence of oxide

Irradiation of CH_3CHO/PBN solutions. Prior to the irradiation of powder suspensions, a series of neat aldehyde irradiations were performed in order to aid in the identification of radical adducts formed in the heterogeneous process. No PBN adducts were generated in the dark, irrespective of the state of oxygenation of the solution.

Fig. 2(A) shows the PBN adduct spectrum obtained from a 600 W irradiation of acetaldehyde ($a_N = 14.32$ G, $a_H = 2.17$ G), displaying the triplet of doublets structure typical of PBN adducts of aliphatic and aromatic radicals. The same adduct spectrum is produced in both oxygenated and deoxygenated solution, indicating that this adduct is not an oxidative product. The signal intensity reaches a maximum following only 8–10 s of irradiation. Scheme 2 illustrates the possible photoscission products arising from a broad band UV irradiation of acetaldehyde[21] by (*a*) primary photodissociation and (*b*) oxidation of primary products. Table 1 lists the hyperfine parameters for PBN adducts obtained in this study and studies by other authors. Comparison of our values with the list of PBN adduct parameters given in Table 1 indicates that this adduct is best attributed to trapped formyl radicals [eqn. (5)] or some

Table 1 Hyperfine parameters for PBN adducts obtained in this and other studies

Species adducted	a_N/G	a_H/G	Solvent	Ref.
$H\cdot$ (hydrogen)	15.30	8.20	CH_2Cl_2	32
$HO\cdot$ (hydroxyl)	15.30–15.60	2.60–2.70	H_2O	33
$\cdot CH_2CHO$ (C-centered)	14.80	3.40	Acetaldehyde	31
$CH_3CO\cdot$ (acetyl)	14.0	3.0	2-Methylpropane	22
$CH_3\cdot$ (methyl)	14.91	3.66	Toluene	34
$CH_3CH_2O\cdot$ (ethoxy)	14.40	2.60	Ethanol	30
$CH_3(\cdot CH)OH$ (C-centered)	15.40	3.60	Ethanol	35
$CH_3CO_2\cdot$ (acetoxyl)	13.40	1.40	CH_2Cl_2	25
$\cdot CH_2CH_2OH$ (C-centered)	14.66	3.58	Ethanol	34
PBN–Ox (paramagnetic)	7.95	N/A	CCl_4	26
PBN–O· (PBN–oxy radical)	15.80	2.0	H_2O	33
PBN· (PBN radical)	16.20	3.7	H_2O	33
$CHO\cdot$ (formyl or PBN·)	14.32	2.17	Acetaldehyde	[a]
$CH_3CO_2\cdot$ (acetoxyl)	13.39	1.88	Acetaldehyde	[a]
$CH_3CO\cdot$ (acetyl)	14.28	3.35	Acetaldehyde	[a]
PBN–Ox (paramagnetic)	7.96	N/A	Acetaldehyde	[a]
$CH_3CH_2O\cdot$ (ethoxy)	14.38	3.00	Ethanol	[a]
$CH_3CH_2O\cdot$ (ethoxy)	14.37	3.00	50:50 v/v EtOH–acetaldehyde	[a]

[a] This study.

photodegradative product of the spin trap itself. Since neither has been reported previously in acetaldehyde solvent, a confident assignment of this species remains somewhat elusive. However, this result does aid in the identification of other adducts reported in this study by ruling out the adduction of the formyl radical in ambient light experiments. This result also demonstrates the uncertainties associated with the assignment of radical species formed during the high energy irradiation of spin trap solutions: UV irradiation ($\lambda < 350$ nm) of solutions of the spin trap DMPO have been previously reported to result in the formation of paramagnetic dimers of the photoexcited spin trap.[8]

The spectrum of the adduct produced during a 20 min ambient light irradiation of deoxygenated acetaldehyde is shown in Fig. 2(B) ($a_N = 14.28$, $a_H = 3.35$). The signal intensity reaches a maximum following 25–30 min of irradiation. Because the solution is deoxygenated in this case, no peroxyacyl radicals are trapped [eqn. (8)]. It is also highly unlikely that photodissociations leading to the formation of $\cdot CH_2CHO$ [eqns. (5) and (6)] are occurring at any appreciable rate, since there is insufficient solar output at the high energies required. The spectrum in Fig. 2(B) can be assigned to the presence of trapped acetyl radicals generated in the process represented by eqn. (7). The spin adduct parameters of PBN–acetyl adducts have been previously reported, in 2-methylpropane solvent, as $a_N = 14.0$ G and $a_H = 3.0$ G.[22] Signal intensities in all ambient photolyses of neat acetaldehyde are approximately two orders of magnitude lower than in the case of high power UV photolysis, probably because of the higher photon intensities used in the lamp photolysis.

The EPR spectrum of the adducts formed during the ambient light photolysis of oxygenated acetaldehyde is shown in Fig. 2(C) ($a_N = 13.39$ G, $a_H = 1.88$ G). Arguments previously articulated above rule out the adduction of adducts arising as a result of high energy photoscissions. The adduct parameters in Fig. 2(C) differ markedly from those measured following the irradiation of deoxygenated solutions, indicating that the adducted species in this instance is an oxidative product. Inspection of eqns. (7) and (8) indicates that the initial radical product of the reaction between ambient light irradiated acetaldehyde and O_2 is a peroxyacyl species ($CH_3CO_3\cdot$), which has long been proposed by many authors as an intermediate in the autoxidation of aldehydes.[23,24] In view of the inherent instability of peroxyacetyl radicals, the total absence of any reported PBN–peroxyacetyl adduct parameters is unsurprising. We conclude that Fig. 2(C) represents the PBN adduct spectrum of acetoxyl radicals ($CH_3CO_2\cdot$) generated *via* decomposition of the peroxyacetyl species. Table 1 shows the close agreement with PBN–acetoxyl adduct parameters reported by Pryor *et al.*[25] in CH_2Cl_2 solvent.

3.2 Radicals generated in the presence of oxide

3.2.1 Irradiation of uncoated TiO_2 powder suspensions. No PBN radical adducts were detected from acetaldehyde/TiO_2 powder suspensions kept in the dark. Irradiation of suspensions at 600 W UV power resulted once again in the spectrum shown in Fig. 2(A); the assignment of this adduct is discussed in section 3.1. The extent of oxygenation of the solution has no effect upon the spectrum generated by 600 W irradiation of acetaldehyde/TiO_2 suspensions.

The spectrum generated during a 20 min ambient light irradiation of oxygenated acetaldehyde/TiO_2 suspension is shown in Fig. 3(A). Three paramagnetic species are evident, labelled (*a*), (*b*) and (*c*). The weak signal exhibiting a single coupling to nitrogen ($a_N = 7.96$ G) is the well known paramagnetic form of oxidised PBN (PBN–Ox),[26] and—in this study—is seen only in the ambient irradiation of oxygenated powder suspensions. A minor species of $a_N \approx 14$ G is also present. The concentration of this secondary adduct is too low for an accurate determination of its hyperfine parameters. However, the observation that this signal disappears when the irradiation is performed under anaerobic conditions suggests that the adduction of acetoxyl radicals is responsible for this adduct.

The primary adduct in Fig. 3(A) has almost identical hyperfine parameters to those reported for the ambient irradiation of neat deoxygenated acetaldehyde/PBN solution [Fig. 2(B)]. This signal is assigned to the trapping of acetyl radicals arising as a result of some heterogeneously assisted photoprocess occurring at the solid–liquid interface. The trapping of acetyl radicals as the primary species in oxygenated solution is most likely due to two independent effects. The initial products of acetyl radical oxidation are peroxyacetyl radicals, which have never been previously trapped due to their intrinsic instability. For example, $k_{\text{(fragmentation)}}$ at 300 K for peroxyacetyl radicals is $>10^{10}$ s^{-1} compared to *ca.* 7 s^{-1} for acetyl radicals.[27] Inspection of eqn. (9) also reveals that the reaction of peroxyacetyl radicals with acetaldehyde yields acetyl radicals as the only paramagnetic products. It is then likely that acetyl radicals trapped in oxygenated suspension are generated *via* the two different reaction routes given in eqns. (7) and (9), resulting in the oxidative product appearing as the secondary adduct in the EPR spectrum. Separation of solution from powder by centrifugation, and subsequent measurement of spin adduct concentration in the separated phases, gives a solution signal only four times as intense as the powder signal, indicating that there is some tendency for the PBN spin adducts to accumulate at the powder surface. This observation suggests that the lower signal intensity, for oxidative products in the mixed adduct spectrum, is due to the concentration of spin trap at the solid–liquid interface, where acetyl radicals would be preferentially trapped. Soria *et al.*[8] have also reported the aggregation of spin adducts of DMPO at TiO_2 surfaces.

The primary radical adduct signal in Fig. 3(A) is found consistently to be some thirty times more intense than that assigned to the trapping of acetyl radicals in ambient irradiations of neat acetaldehyde. This result is considered unusual in view of the reported discontinuation of the heterogeneous photocatalytic process in TiO_2/aliphatic aldehyde systems, when the aldehyde becomes predominant in light absorption.[14] Clearly, given that band gap transitions play no part in aliphatic aldehyde photocatalysis at high aldehyde concentrations, the process leading to formation of radical intermediates in this instance must involve a surface assisted decomposition of photoexcited substrate molecules located near the surface region. These observations serve to reaffirm the concerns of Turchi and Ollis,[28] who reported the difficulties associated with attempting to distinguish between the reaction of radicals formed following substrate adsorption and the reaction of radicals located close to the TiO_2 surface.

3.2.2 Irradiation of TiO_2 ($AlPO_4$ coated) and MgO powder suspensions. In order to test the hypothesis that no semiconductor mediated electron transfer occurs when the upper limit for aldehyde concentration is exceeded, powder suspensions in which the band gap activated process would be effectively quenched were studied; $AlPO_4$ coated TiO_2 and uncoated MgO. $AlPO_4$ coating of TiO_2 prevents the photoexcited charge carriers of the semiconductor from reaching the surface of the material, thus preventing the transfer of electrons across the solid–liquid interface. Ambient light irradiation of $AlPO_4$ coated TiO_2 also produces qualitatively the spectrum shown in Fig. 3(A). The signal intensity of the primary acyl adduct arising from the irradiation of the coated material is 0.6 times less intense than that observed for irradiation of uncoated TiO_2. This difference may be, in part, due to a higher degree of aggregation taking place in the coated powder as a result of differences in surface charge between coated and uncoated TiO_2 samples. However, this explanation cannot account for the whole of the 40% loss in signal intensity observed. The degree of PBN oxidation is also reduced significantly when the $AlPO_4$ coated material is used to sensitise the photoreaction of acetaldehyde.

Ambient light irradiation of acetaldehyde/MgO suspension also results in the production of acetyl radicals [Fig. 3(B)]. The primary adduct signal is now three times as intense as that recorded during the ambient irradiation of uncoated TiO_2 suspension. The signal intensities of both the secondary adduct and PBN–Ox are also significantly increased when compared to Fig. 3(A), indicating that the rate of both oxidative processes is enhanced. The observation that the production of all radical species is greatest in irradiated MgO suspensions demonstrates unequivocally that band gap transitions are not responsible for the observed photochemistry; the promotion of an electron across the MgO band gap (7.8 eV) requiring the absorption of a photon with $\lambda \leqslant 160$ nm.[29]

A clear trend emerges in the relationship between extent of radical production/spin trap oxidation and surface basicity of the oxide studied; the production of both acetaldehyde derived radicals and PBN–Ox increasing along the series representing an increase in surface basicity; TiO_2 ($AlPO_4$ coat), TiO_2, MgO. The relative changes in primary radical adduct signal intensity are 0.6 : 1 : 3 respectively. Such an increase in photocatalytic efficiency with increasing surface basicity of TiO_2 has been reported for aldehyde photoredox reactions mediated by an initial excitation of the semiconductor.[7] However, we are unaware of any previous reports of heterogeneous photoreactions—resulting from an initial excitation of the aldehyde—behaving in a similar manner. The trapping of the same primary adduct species in all three heterogeneous systems studied suggests that there is a common process involved in the formation of acetyl radicals in illuminated acetaldehyde/hydroxylated powder suspensions. We propose that abstraction of the H atom from the carbonyl carrying carbon in a photoexcited acetaldehyde molecule is responsible for acetyl radical formation, even when the band gap mediated photoprocess is shut down. The increase in power of hydrogen abstraction by surface bound OH groups then explains the observed correlation between primary adduct signal intensity and surface basicity.

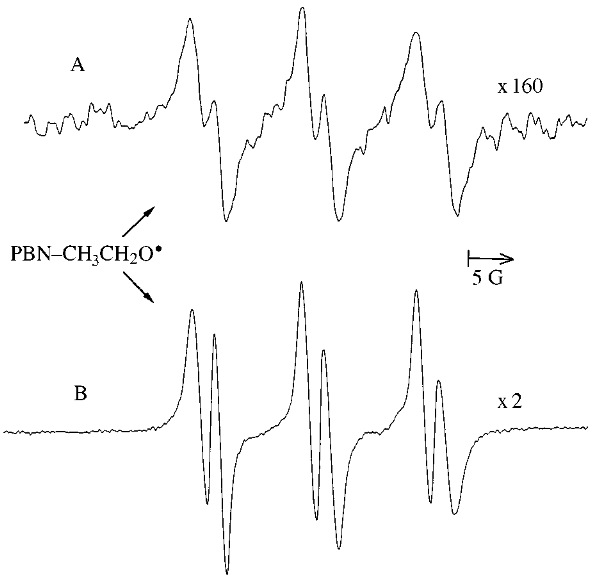


Fig. 4 EPR spectra of PBN spin adducts. (A) 20 min direct sunlight irradiation of TiO_2/ethanol suspension; (B) 20 min direct sunlight irradiation of TiO_2/ethanol suspension.

3.3 Irradiation of $CH_3CHO/CH_3CH_2OH/PBN/TiO_2$ suspensions

In order to investigate the comparative significance of non-band gap mediated aldehyde photochemistry at TiO_2 surfaces, it was necessary to devise spin trapping experiments in which the semiconductor sensitised photocatalytic process is invoked. The TiO_2 photocatalysed reduction of aliphatic aldehydes has been demonstrated as highly efficient when coupled to the concomitant photooxidation of ethanol.[14] However, great care must be taken in controlling the experimental conditions since, under aerobic conditions, some degree of aldehyde oxidation may also occur.

Ambient light photolysis of ethanol/PBN solution did not result in the production of radical adducts. However, ambient light exposure of a TiO_2/ethanol/PBN suspension results in the production of the very weak PBN–adduct spectrum shown in Fig. 4(A) ($a_N = 14.38$ G, $a_H = 3.00$ G). By comparison with the list of adduct values given in Table 1, this adduct is assigned to the trapping of ethoxy radicals.[30] The very low signal intensity is attributed to the absence of a suitable electron acceptor (such as acetaldehyde) which would otherwise retard the rate of electron–hole recombination within the TiO_2. Once again, the same primary adduct is formed irrespective of the amount of dissolved O_2 present. The total signal intensity of ethoxy adducts formed in neat ethanol/TiO_2 suspension is *ca.* 30% of that observed for acetyl adduct formation in neat acetaldehyde/TiO_2 suspension, despite the higher rate of PBN spin adduction for ethoxy radicals reported in this study. This lower reactivity is due partly to the absence of any chromophore within the ethanol molecule, as well as the known lower reactivity of the terminal H atom of ethanol compared with the H atom of the acetaldehyde carbonyl function. Evidently, H abstraction from ethanol then requires a more powerful surface basic site, so that the production of an ethoxy radical—in neat substrate/TiO_2 suspension—requires a more coordinatively unsaturated surface OH group than acetyl radical formation. The failure to detect any radical adducts from the ambient irradiation of neat PBN–ethanol solution is attributed to the absence of a suitable chromophore within the ethanol molecule, indicating that the heterogeneously unaided photodecomposition of ethanol does not occur at any appreciable rate under ambient light conditions. Ambient irradiation of a suspension of deoxygenated TiO_2 in 1 : 1 v/v ethanol–acetaldehyde solution with PBN produces the spectrum shown in Fig. 4(B) which is qualitatively the same PBN–adduct spectrum shown in Fig. 4(A) and assigned to the trapping of ethoxy radicals. The signal intensity of PBN–ethoxy radicals produced from ambient irradiation of acetaldehyde/ethanol/TiO_2 mixture is 80 times greater than that recorded for the ambient irradiation of ethanol/TiO_2. The absence of any acetaldehyde derived PBN–acetyl adducts is due to the higher PBN spin adduction rates reported for alkoxy radicals compared to acyl radicals ($\approx 10^8$ and 10^6 $dm^3\ mol^{-1}\ s^{-1}$, respectively).[35]

Joyce-Pruden *et al.*[14] have reported the production of ethoxy radicals from the UV irradiation of TiO_2/aldehyde/ethanol suspensions, suggesting that the ethoxy radical is one of the most efficient species for preventing electron–hole recombination at the TiO_2 surface. The observed 80 fold increase for the trapping of the same radical adduct, upon addition of acetaldehyde to a suspension of TiO_2 in ethanol, indicates that efficient retardation of electron–hole recombination is taking place. Due to the difference in PBN spin adduction rates for acetyl and ethoxy radicals, a direct comparison between the signal intensities of the acetaldehyde/TiO_2 and acetaldehyde/ethanol/TiO_2 systems is not possible. However, the signal intensity ratio of 1 : 80 observed for ethoxy radicals trapped in ethanol/TiO_2 and ethanol/acetaldehyde/TiO_2 systems suggests that non-band gap mediated processes account for a maximum of only *ca.* 1.25% of radical forming processes in acetaldehyde/ethanol/TiO_2 suspensions irradiated with ambient sunlight. However, neglecting the rate of photon flux and any molecular geometric requirements for the reaction between a photoexcited substrate molecule and $OH_{(surf)}$, it is likely that the substrate initiated process actually accounts for <1.25% of all radical forming processes when interfacial electron transfer is taking place. The rate of substrate initiated process is then directly proportional to the number of photo-activated substrate molecules located close enough to the TiO_2 surface to undergo hydrogen abstraction by OH groups not acting as hole traps. H abstraction by such OH· groups would then be considered a semiconductor sensitised process, occurring with an enhanced rate when the substrate molecule is in the photoexcited state prior to surface interaction. At higher photon fluxes, however, it is conceivable that the pre-adsorption excitation of substrate molecules may make a significant contribution to the overall rate of the heterogeneous photodegradative process.

4. Conclusions

The generation of organic substrate derived radical intermediates in the direct sunlight exposure of TiO_2 suspensions containing acetaldehyde, ethanol and 50 : 50 v/v acetaldehyde–ethanol is confirmed using the spin trapping technique. By carefully controlling the experimental conditions, it is possible to distinguish between the paramagnetic intermediates of oxidative and non-oxidative photolysis. Direct sunlight irradiation of neat deoxygenated acetaldehyde is shown to yield trapped acetyl radicals, whereas irradiation of oxygenated acetaldehyde is believed to result in the trapping of acetoxyl radicals; secondary species formed from the degradation of unstable peroxyacetyl radicals, initial products of the reaction between acetyl radicals and O_2. This information then affords the identification of radical species arising in both types of heterogeneous process reported here. In both processes, the primary intermediates trapped are shown to be acetyl radicals, irrespective of the state of oxygenation of the organic/metal–oxide suspension. The inherent instability of peroxyacetyl species generated in oxygenated suspensions, together with the tendency of spin adducts to accumulate at the solid-solution interface, is held to be responsible for this effect.

Heterogeneous radical forming processes are demonstrated to be greatly enhanced by coupling the photooxidation of ethanol with the concomitant photoreduction of acetaldehyde, thereby facilitating the complete recycling of an electron within the photoexcited semiconductor. Radical formation in the absence of semiconductor mediated electron transfer is believed to arise as a result of the interaction between basic surface OH groups and photoexcited substrate molecules located at the metal oxide surface. The generation of higher concentrations of acetyl radicals in sunlight irradiated MgO/neat acetaldehyde suspensions, compared to irradiation of TiO_2/neat acetaldehyde suspensions, demonstrates unequivocally that no band gap mediated electron transfer is occurring. The enhanced rate of radical production in MgO suspension is most likely due to easier abstraction of aldehydic H atoms, from directly photoexcited aldehyde molecules, by the stronger basic OH groups of the MgO surface. The direct excitation of substrate molecules, *vs.* initial photoexcitation of the semiconductor, is shown to account for the production of only 1–1.25% of all radical intermediates when direct sunlight is used as the photon source. At higher photon fluxes, however, it is possible that such pre-adsorption excitation of substrate molecules may make a significant contribution to the overall process rate.

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