Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 172 (2005) 207–213

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

TiO_2—photocatalyzed oxidation of aniline

C. Karunakaran*, S. Senthilvelan, S. Karuthapandian

Department of Chemistry, Annamalai University, Annamalainagar 608002, India

Received 8 July 2004; received in revised form 4 November 2004; accepted 4 December 2004

Abstract

The photooxidation of aniline to azobenzene on TiO_2 (anatase) in ethanol using solar and UV (365 nm) lights was investigated as a function of [aniline], catalyst loading, airflow rate, solvent composition, etc. The catalyst shows sustainable photocatalytic activity. The photocatalysis is larger with illumination at 254 nm than at 365 nm. Electron donors like triphenylphosphine, diphenylamine and hydroquinone facilitate the oxidation. Azide ion, a singlet oxygen quencher, fails to inhibit the catalysis. The photooxidation occurs in a number of organic solvents. The mechanism of photocatalysis is discussed and the product formation analyzed using a kinetic model.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Photooxidation; Aniline; Sunlight; UV light; TiO_2

1. Introduction

The application of photosemiconductors to convert light to electrical energy [1,2], to mineralize toxic chemicals [3], to organic synthesis [4,5] and to bactericidal activity [6] continues to be of interest. TiO_2 is the widely used semiconductor photocatalyst due to its non-toxic nature, chemical stability, availability, low cost, and capability of repeated use without substantial loss of catalytic activity [7]. Also, its surfaces have been extensively examined [8]. However, one disadvantage is its bandgap energy (~3.2 eV) requiring UV-illumination for photoactivation. Doping of TiO_2 with metal ions [9] and use of dye-sensitizers [10,11] improve the performance of TiO_2 as a photocatalyst and extend its light absorption and conversion capacity to the visible portion of the solar spectrum. But the problem with the metal doped and dye-sensitized TiO_2 in organic synthesis is the cost and reuse; dye-sensitizers are only adsorbed over the photocatalyst. Solar UV light reaching the surface of the earth and available to excite TiO_2 is relatively small (ca. 3–5%) but as the energy is free of cost and abundant its use is of interest. Review of literature reveals only a few preliminary studies with natural sunlight [12–14]. Here we report, for the first time, the results of solar photocatalysis; the problem of fluctuation of sunlight intensity even under clear sky during the period of the experiment is overcome by carrying out set of experiments simultaneously and comparing the results. The UV-irradiation of air-equilibrated solution of aniline yields azobenzene with benzophenone sensitizing the oxidation [15,16]. The UV-irradiated ZnO also brings in the photooxidation [17,18]. At very low concentration, ppm level, aniline undergoes photocatalytic degradation on TiO_2 immobilized on porous nickel [19].

2. Experimental

2.1. Materials

TiO_2 (Merck) used is of anatase form (99%+); the XRD pattern of the sample totally matches with the standard pattern of anatase (JCPDC) and the rutile lines are insignificant (Siemens D-5000 XRD, Cu Kα X-ray, $\lambda = 1.54$ Å, scan: 5–60°, scan speed: $0.2^\circ\, s^{-1}$). Its BET surface area was determined as $14.68\, m^2\, g^{-1}$ and the particle sizes were measured using Easy particle sizer M1.2, Malvern Instruments (focal length 100 mm, beam length 2.0 mm,

---

* Corresponding author. Tel.: +91 4144 221820; fax: +91 4144 238145.
E-mail address: karunakaranc@rediffmail.com (C. Karunakaran).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.12.010

wet (methanol) presentation) as 27.6, 23.8, 20.5, 17.7, 9.8, 8.5, 7.3, 4.1, 3.5, 3.0, 2.6 μm at 9.1, 18.0, 15.0, 1.4, 12.1, 17.7, 10.5, 1.2, 4.6, 6.5, 2.0%, respectively. Aniline, AR was distilled before use. Commercially available ethanol was distilled over calcium oxide; other organic solvents were of LR grade and distilled prior to use.

2.2. Solar photooxidation

The solar photocatalyzed reaction was carried out under clear sky from 10.30 a.m. to 12.30 p.m. in summer (March–July). The intensity of solar radiation was measured using Global pyranometer, MCPT, supplied by Industrial Meters, Bombay. Fresh solutions of aniline of desired concentrations were taken in wide cylindrical glass vessels of uniform diameter and appropriate height; the entire bottom of the vessel was covered by the catalyst. Air was bubbled using a micropump without disturbing the catalyst bed. The volume of the reaction solution was kept as 25 mL and the loss of solvent due to evaporation was compensated periodically. An amount of 1 mL of the reaction solution was withdrawn at regular intervals, diluted five times and the absorbance measured at 344 nm using Hitachi U-2001 or Jasco UVIDEC-340 UV–vis spectrophotometer.

2.3. UV photooxidation

Photooxidation studies with UV light were carried out in a Heber multilamp photoreactor (HML MP88) fitted with eight 8 W mercury UV lamps of wavelength 365 nm (Sankyo Denki, Japan) and highly polished anodized aluminum reflector; the sample was placed at the centre. Four cooling fans at the bottom of the reactor dissipate the heat generated. The reaction tube was borosilicate glass tube of 15 mm inner diameter. Photooxidation was also carried out in a Heber microphotoreactor (HMI SL W6) fitted with a 6 W 254 nm low-pressure mercury lamp and a 6 W 365 nm mercury lamp. Quartz and borosilicate glass tubes were used for 254 and 365 nm lamps, respectively. The photon flux of the light source (I_0) was determined by ferrioxalate actinometry.

The volume of the reaction solution was always maintained as 25 mL in the multilamp photoreactor and 10 mL in the micro reactor. Air was bubbled through the reaction solution that effectively stirs the solution and keeps the suspended catalyst under constant motion. The absorbance was measured at 344 nm after centrifuging the catalyst and diluting the solution five times to keep the absorbance within the Beer–Lambert's law limit.

2.4. Product analysis

Solar photooxidation of aniline in ethanol on TiO_2 yields azobenzene as the only product. The GC-mass, IR and UV–vis spectra of the extracted solid product are identical with those of *trans*-azobenzene (Fluka).

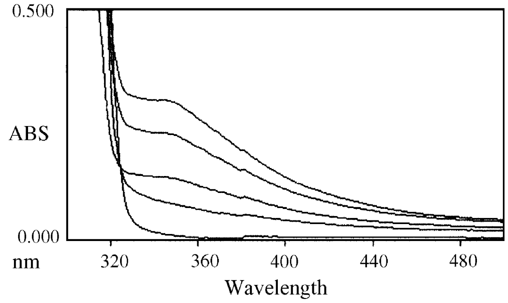

Fig. 1. Solar photooxidation of aniline in ethanol on TiO_2. The UV–vis spectra of the reaction solution diluted five times and recorded at 0, 30, 60, 90 and 120 min (↑); [aniline] = 0.113 M, TiO_2 bed = 12.5 cm^2, weight of TiO_2 = 1.0 g, airflow rate = 4.75 mL s^{-1}, volume of reaction solution = 25 mL.

2.5. Product estimation

In solar photocatalysis as well as that with UV light, the UV–vis spectra of the reaction solution recorded during the course of the reaction are similar (Fig. 1; $\lambda_{max} = 344$ nm) but not identical with that of the extracted product ($\lambda_{max} = 434$ nm). This is due to the formation of both *cis*- and *trans*-azobenzenes during the course of the reaction and the unstable *cis* form (*Z*) transforms to the *trans* form (*E*) slowly on standing. The UV–vis spectrum of the irradiated reaction solution allowed to stand for a couple of days in dark is identical with that of the authentic *trans*-azobenzene confirming the slow transformation of the unstable *cis* form to *trans* form. For a solution of *cis*- and *trans*-azobenzenes it can be shown that

$$[E] = (\text{abs}_{281}\varepsilon_{Z(433)} - \text{abs}_{433}\varepsilon_{Z(281)})/ (\varepsilon_{E(281)}\varepsilon_{Z(433)} - \varepsilon_{Z(281)}\varepsilon_{E(433)})$$

and

$$[Z] = (\text{abs}_{281}\varepsilon_{E(433)} - \text{abs}_{433}\varepsilon_{E(281)})/ (\varepsilon_{Z(281)}\varepsilon_{E(433)} - \varepsilon_{Z(433)}\varepsilon_{E(281)})$$

where ε is the corresponding molar extinction coefficient. Calculation of the ratio $[E]/[Z]$ using the above equations, the experimentally determined $\varepsilon_{E(433)}$ and $\varepsilon_{E(281)}$, the reported $\varepsilon_{Z(433)}$ and $\varepsilon_{Z(281)}$ and the measured absorbance of the reaction solution at 433 and 281 nm at different reaction times shows that the ratio remains practically the same (1.85) during the course of the photooxidation followed. The total concentration of azobenzene, $([E] + [Z]) = \{1 + ([E]/[Z])\}\text{abs}_{344}/\{\varepsilon_{Z(344)} + \varepsilon_{E(344)}([E]/[Z])\}$; $\varepsilon_{E(344)}$ was determined experimentally and $\varepsilon_{Z(344)}$ calculated from the measured abs_{344}; $\text{abs}_{344} = \{\varepsilon_{Z(344)} + \varepsilon_{E(344)} ([E]/[Z])\}[Z]$.

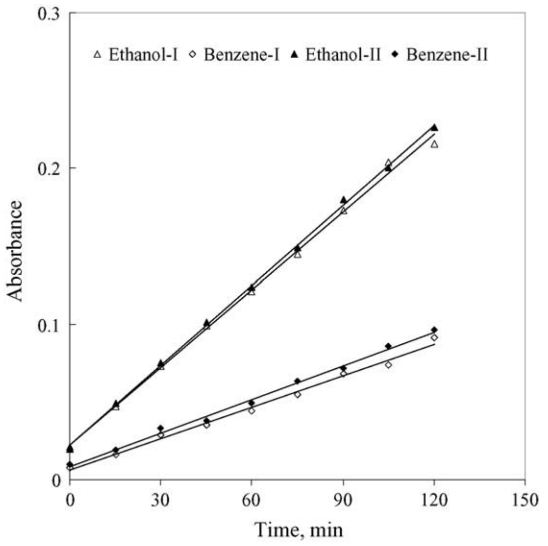

Fig. 2. Solar photooxidation of aniline in ethanol and benzene on TiO_2. Absorbance–time plots (experiments in each set conducted simultaneously and sets I and II on different days; the reaction solution diluted five times prior to absorbance measurements); [aniline] = 0.113 M, TiO_2 bed = 12.5 cm^2, weight of TiO_2 = 1.0 g, airflow rate = 4.75 mL s^{-1}, volume of reaction solution = 25 mL.

3. Results and discussion

3.1. Obtaining solar oxidation results

The measurement of solar radiation shows fluctuation of sunlight intensity ($530 \pm 40\,W\,m^{-2}$) during the photooxidation even under clear sky. Now, for the first time, identical sunlight intensity was maintained for a set of photooxidation experiments of desired reaction conditions by carrying out the experiments simultaneously, thus making possible the comparison of the solar results. The solar photooxidation results are reproducible. Fig. 2 is the linear increase of the absorbance of the reaction solution with the reaction time, one set of experiments conducted in ethanol and benzene side by side on 1 day and the other set similarly on another day. The ratio of the slopes of the absorbance–time profiles of the reactions in ethanol and benzene remains the same (2.4) although the experiments were conducted on two different days, obviously under different sunlight intensities. This reproducibility is not surprising as the fluctuation of sunlight intensity is identical in test and control (standard) experiments and the ratio turns out to be independent of fluctuation of intensity. Further, the results of a pair of experiments carried out simultaneously confirm the reproducibility of the rates of solar photocatalysis. Fig. 3 presents the solar photoformation of azobenzene in ethanol under identical conditions and conducted simultaneously. The ratio of the rates obtained from the linear plots is unity (1.01).

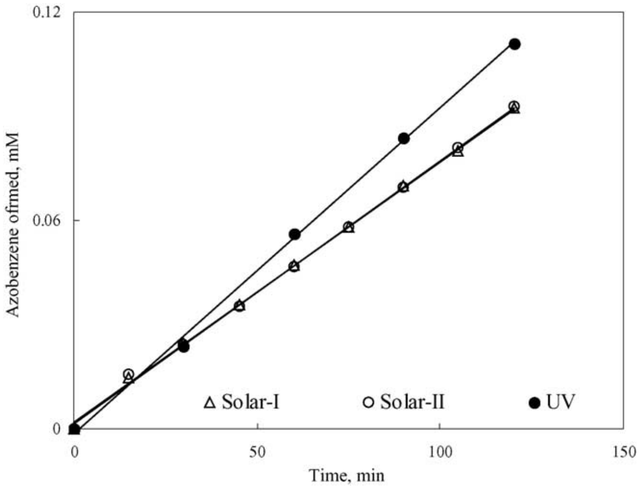

Fig. 3. Photoformation of azobenzene in ethanol on TiO_2; [aniline] = 0.113 M, weight of TiO_2 =1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 mL s^{-1}; solar: TiO_2 bed = 12.5 cm^2; UV: λ = 365 nm, $I_0 = 2.46 \times 10^{-5}$ einstein $L^{-1}\,s^{-1}$.

3.2. Factors influencing solar photocatalysis

The influence of various factors on the solar photocatalysis in ethanol was studied by carrying out the required set of experiments simultaneously; the data in each figure correspond to a set of photocatalytic experiments made simultaneously. The least squares slope of the linear plot of [azobenzene] versus time (e.g. Fig. 3) affords the rate of formation of azobenzene. Experiments at different concentrations of aniline shows that the reaction rate increases with [aniline] (Fig. 4) and the variation is according to the Langmuir–Hinshelwood model [20]. The double reciprocal plot of rate versus [aniline] yields a straight line with a positive y-intercept. The variation of the amount of TiO_2 spread

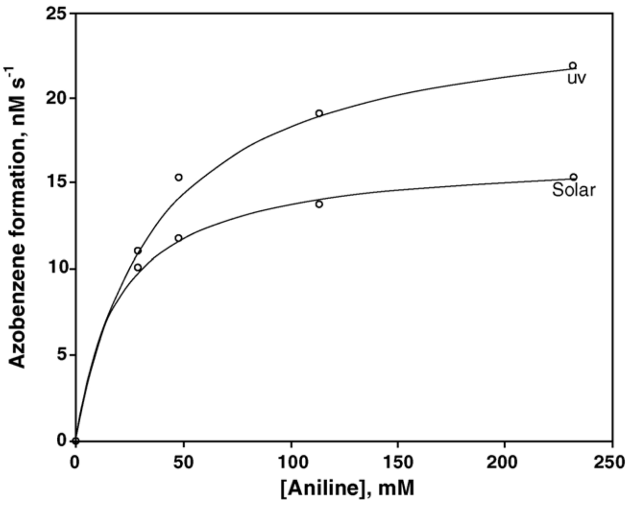

Fig. 4. Azobenzene formation in ethanol on TiO_2 at different [aniline]; weight of TiO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 (solar), 7.8 (UV) mL s^{-1}; solar: TiO_2 bed = 12.5 cm^2; UV: λ = 365 nm, $I_0 = 2.46 \times 10^{-5}$ einstein $L^{-1}\,s^{-1}$.

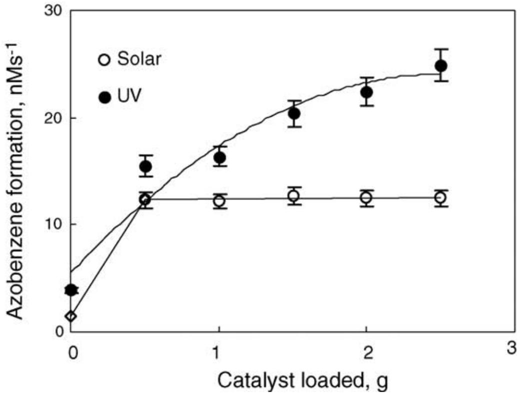

Fig. 5. Azobenzene formation in ethanol at different amounts of TiO_2 loading; [aniline] = 0.113 M, volume of reaction solution = 25 mL, airflow rate = 4.75 (solar), 7.8 (UV) mL s^{-1}; solar: TiO_2 bed = 12.5 cm^2; UV: $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein L^{-1} s^{-1}.

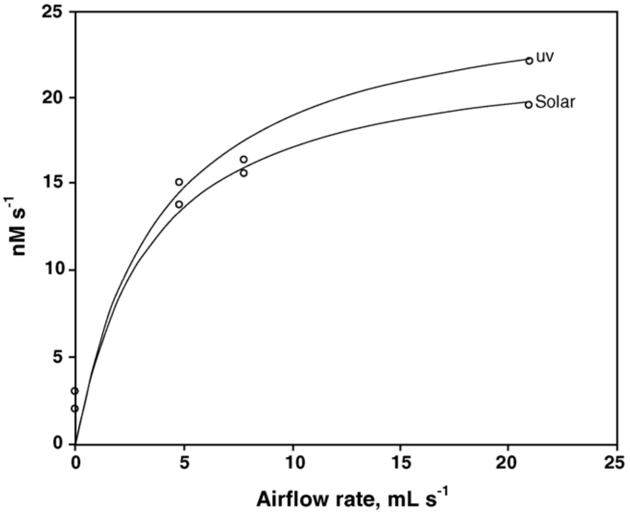

Fig. 7. Azobenzene formation in ethanol on TiO_2 at different airflow rates: [aniline] = 0.113 M, weight of TiO_2 = 1.0 g, volume of reaction solution = 25 mL; solar: TiO_2 bed = 12.5 cm^2; UV: $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein L^{-1} s^{-1}.

at the bottom of the reaction vessel (catalytic bed) does not lead to any appreciable change in the photooxidation rate (Fig. 5); the bottom of the cylindrical reaction vessel was fully covered by the catalyst in all the cases and the increase of the amount of TiO_2 does not result in increase of the area of the catalyst bed but only leads to increased thickness of the TiO_2 bed. In the absence of the photocatalyst, the reaction is an uncatalyzed one and hence is weak. The photoformation of azobenzene increases linearly with the apparent area of the catalyst bed (Fig. 6). Study of the photooxidation as a function of airflow rate shows enhancement of photocatalysis by oxygen (Fig. 7). The variation of reaction rate with the airflow rate suggests Langmuir–Hinshelwood kinetics and the linear double reciprocal plot of reaction rate versus airflow rate confirms the same. The reaction was also studied without bubbling air but the solution was not deaerated. The dissolved oxygen itself brings in the oxidation but the photocatalysis is slow. The reaction does not take place in dark. The photocatalyst does not lose its catalytic activity on repeated use. Reuse of the photocatalyst yields identical results. Addition of water to the reaction medium slows down the reaction (Fig. 8). Electron donors like triphenylphosphine (TPP), hydroquinone (HQ) and diphenylamine (DPA), favor the photoformation of azobenzene. However, triethylamine (TEA) fails to do so. Addition of TEA (0.281 M) to the reaction solution results in an increase of azobenzene formation rate only by ca. 15%. The variation of the enhanced photoformation rate (the difference in the rates of formation of azobenzene in the presence and absence of electron donors) with [TPP], [HQ] and [DPA] (Fig. 9) reveals Langmuir–Hinshelwood kinetics and the linear double reciprocal plots of the enhanced rate versus [TPP], [HQ] and [DPA] confirm the same. Use of sacrificial electron donors leads to hole trapping resulting in enhanced photocatalysis [4]. Anionic as well as cationic surfactants influence the photocatalysis only marginally; addition of anionic surfactants aerosol OT (sodium bis-2-ethylhexyl sulfosuccinate, 0.0225 M) and sodium lauryl sulfate (SLS, 0.0347 M) and cationic surfactant

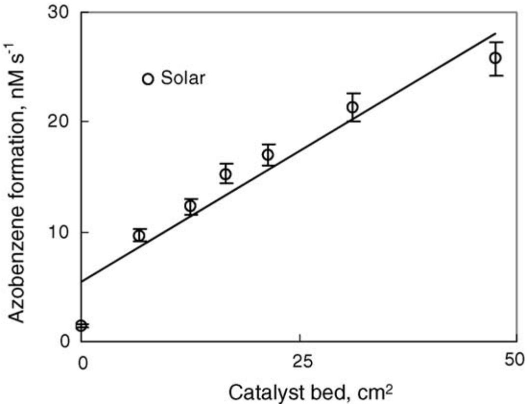

Fig. 6. Azobenzene formation (solar) in ethanol at varying areas of TiO_2 bed; [aniline] = 0.113 M, weight of TiO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 mL s^{-1}.

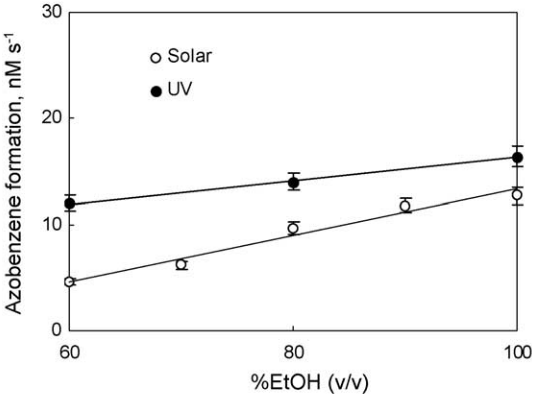

Fig. 8. Azobenzene formation on TiO_2 in aq. EtOH; [aniline] = 0.113 M, weight of TiO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 (solar), 7.8 (UV) mL s^{-1}; solar: TiO_2 bed = 12.5 cm^2; UV: $\lambda = 365$ nm, $I_0 = 2.46 \times 10^{-5}$ einstein L^{-1} s^{-1}.

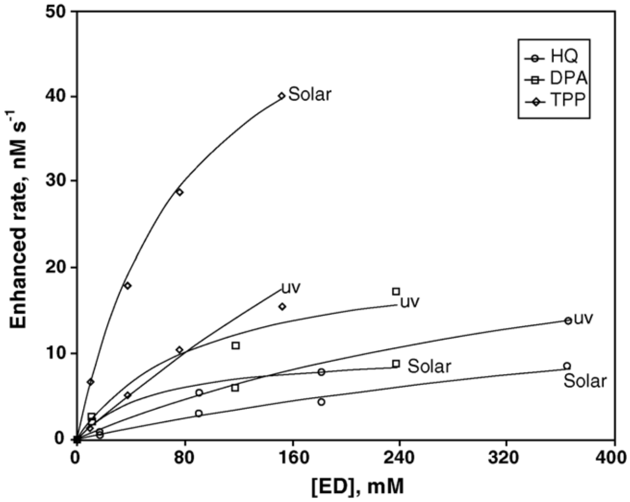

Fig. 9. Azobenzene formation in ethanol on TiO_2 in presence of electron donors (ED); [aniline] = 0.113 M, weight of TiO_2 = 1.0 g, volume of reaction solution = 25 mL, airflow rate = 4.75 (solar), 7.8 (UV) mL s^{-1}; solar: TiO_2 bed = 12.5 cm^2; UV: λ = 365 nm, $I_0 = 2.46 \times 10^{-5}$ einstein L^{-1} s^{-1}.

cetyltrimethylammonium bromide (CTAB, 0.0274 M) to the reaction solution increases the photoformation rate by 13, 26 and 18%, respectively. Vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) neither suppress the photocatalysis nor undergo polymerization indicating the absence of free radicals in the reaction solution during the course of photocatalysis.

3.3. Factors influencing UV photocatalysis

The TiO_2-photocatalyzed oxidation of aniline in ethanol in the presence of air was studied using a multilamp photoreactor with mercury UV lamps of wavelength 365 nm. Linear increase of azobenzene-concentration with illumination time affords the photochemical formation rate (e.g. Fig. 3) and the rates are reproducible within ±6%. Rate measurements at different [aniline] show increase of the oxidation rate with [aniline] (Fig. 4) and the increase is according to Langmuir–Hinshelwood kinetics. The increase of the amount of TiO_2 suspended in the reaction medium leads to increased azobenzene formation but the rate reaches a limit at high catalyst loading (Fig. 5). Study of the photooxidation as a function of airflow rate reveals enhancement of photocatalysis by oxygen and the variation of the reaction rate with flow rate conforms to the Langmuir–Hinshelwood model (Fig. 7). Also, the reaction was studied without bubbling air but the solution was not deoxygenated. The dissolved oxygen itself brings in the oxidation but the photocatalysis is slow. The photooxidation was examined as a function of light intensity. The oxidation was carried out with eight, four and two lamps, the angles sustained by the adjacent lamps at the sample are 45, 90 and 180°, respectively. Fig. 10 presents the variation of rate with the light intensity. The reaction does not occur in dark. Investigation of the photocatalysis using a 6 W 365 nm mercury lamp ($I_0 = 1.81 \times 10^{-5}$ einstein L^{-1} s^{-1}) and a 6 W 254 nm low-pressure mercury lamp ($I_0 = 5.22 \times 10^{-6}$ einstein L^{-1} s^{-1}) separately in the micro reactor under identical conditions reveals that high energy radiation is more effective in bringing out the photocatalysis. Azobenzene formed in 10 min on illumination at 365 and 254 nm are 21 and 73 μM, respectively ([aniline] = 0.113 M, TiO_2 suspended = 0.20 g, airflow rate = 7.8 mL s^{-1}, volume of reaction solution = 10 mL). The metal oxide does not lose its photocatalytic activity on illumination. Reuse of the catalyst reveals sustainable photocatalytic efficiency. Addition of water to the reaction solution suppresses the photocatalysis (Fig. 8). Electron donors like triphenylphosphine, hydroquinone and diphenylamine enhance azobenzene formation. The variation of the enhanced photocatalysis rate with [TPP], [HQ] and [DPA] suggests Langmuir–Hinshelwood kinetics (Fig. 9). However, triethylamine (0.287 M) fails to facilitate azobenzene formation (reaction conditions as in Fig. 9). Anionic and cationic surfactants (0.0225 M aerosol OT, 0.0347 M SLS, 0.0274 M CTAB) influence the photocatalysis with UV light only marginally; the rate enhancements are 7, 31 and 16%, respectively. Also, vinyl monomers like acrylonitrile (0.608 M) and acrylamide (0.141 M) do not inhibit the photocatalysis. Nor do they polymerize. Azide ion (0.154 M), a singlet oxygen quencher, fails to suppress the formation of azobenzene indicating the absence of involvement of singlet oxygen in the photocatalysis.

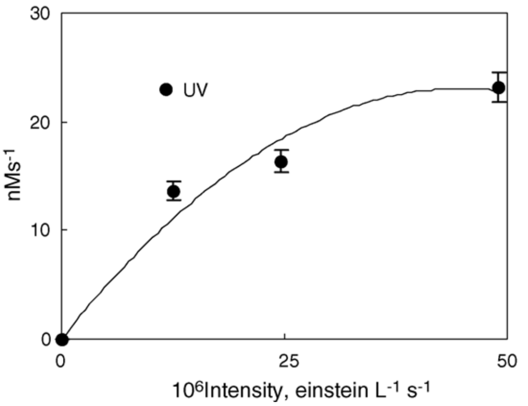

Fig. 10. Azobenzene formation in ethanol on TiO_2 at different light intensities; [aniline] = 0.113 M, TiO_2 suspended = 1.0 g, airflow rate = 7.8 mL s^{-1}, λ = 365 nm, volume of reaction solution = 25 mL.

3.4. Mechanism

The bandgap energy of TiO_2 is 3.2 eV [7] and illumination of the semiconductor with light of energy greater than the bandgap results in bandgap excitation of the semiconductor leading to creation of electron–hole pairs; holes in the valence band and electrons in the conductance band. Since the recombination of photogenerated electron–hole pairs in semiconductors are so rapid (occurring in a picosecond time scale), for an effective photocatalysis the reactants are to be adsorbed on the photocatalyst [7]. The hole reacts with adsorbed aniline molecule to form aniline radical-cation ($PhNH_2^{\bullet+}$). In the presence of oxygen, transfer to the adsorbed oxygen molecule resulting in highly active superoxide radical-anion, $O_2^{\bullet-}$, effectively removes the electron [4]. The reaction of aniline radical-cation with superoxide radical-anion results in nitrosobenzene. Condensation of nitrosobenzene with aniline, present in large excess, yields azobenzene

$$SC + h\nu \rightarrow h_{(vb)}^{+} + e_{(cb)}^{-}$$

$$PhNH_{2(ads)} + h_{(vb)}^{+} \rightarrow PhNH_2^{\bullet+}$$

$$O_{2(ads)} + e_{(cb)}^{-} \rightarrow O_2^{\bullet-}$$

$$PhNH_2^{\bullet+} + O_2^{\bullet-} \rightarrow PhNO + H_2O$$

$$PhNO + PhNH_2 \rightarrow PhNNPh + H_2O$$

The mechanism of the heterogeneous photocatalysis is based on the adsorption of aniline at the surface of titania; amino group is most likely hydrogen bonded to the titania oxygen. At high aniline concentration, the catalyst surface is saturated with the substrate, thus enabling the intermediate formed to react with another aniline molecule yielding the condensed product. This is in agreement with the reported photodegradation of aniline on titania immobilized on porous nickel when present at ppm level [19]. Ethanol may undergo oxidation in the presence of illuminated semiconductor and generation of radicals is possible [21,22]. If the photooxidation of aniline were due to the radicals generated from solvent ethanol, contrary to the experimental observations, azobenzene formation should not depend on [aniline]; the photogenerated radicals are short lived and react almost instantaneously demanding non-dependence of the reaction rate on [aniline]. Also, the oxidation occurs in a number of organic solvents (vide infra).

3.5. Kinetic analysis

The kinetic law that governs heterogeneous photocatalyzed reaction in a continuously stirred tank reactor (CSTR) [23] is $\text{rate} = kK_1K_2SI_0C[PhNH_2]\gamma/(1+K_1[PhNH_2])(1+K_2\gamma)$, where K_1 and K_2 are the adsorption coefficients of aniline and oxygen on TiO_2, k the specific rate of oxidation of aniline, γ the airflow rate, S the specific surface area of TiO_2, C the amount of TiO_2 suspended per liter and I_0 the light intensity expressed in einstein $L^{-1}\,s^{-1}$. Linear double reciprocal plots of rate of azobenzene formation versus (i) $[PhNH_2]$ and (ii) airflow rate are in agreement with the kinetic law and afford the adsorption coefficients as $K_1 = 78\,L\,mol^{-1}$, $K_2 = 0.31\,mL^{-1}\,s$, $k = 3.4\,\mu mol\,L\,m^{-2}\,einstein^{-1}$. The data fit to the curves (Figs. 4 and 7), drawn according to the above rate expression using a computer program supports the kinetic law. However, the rate of photocatalysis fails to vary linearly with the amount of TiO_2 suspended. This is because of the high catalyst loading. At high catalyst loading, the surface area of the catalyst exposed to illumination does not commensurate with the weight of the catalyst. The amount of TiO_2 employed is beyond the critical amount corresponding to the volume of the reaction solution and reaction vessel; the whole amount of TiO_2 is not exposed to illumination. The photocatalysis lacks strict linear dependence on illumination intensity; less than first power dependence of surface-photocatalysis rate on light intensity at high intensity is well known [24].

3.6. Photocatalysis in different solvents

Adsorption of aniline and oxygen on titania and the concentration of dissolved oxygen in the reaction medium vary with the solvent, thus influencing the photocatalysis. The variation of the photocatalysis rate with the solvent is also likely due to the band bending at the semiconductor–solution interface [7]. The oxidation of aniline on TiO_2 with sunlight and UV irradiation was carried out in 18 solvents and the UV–vis spectra reveal formation of azobenzene in all the solvents studied. The least-squares slopes of the linear absorbance–time traces of photocatalysis with UV light are 40.3, 49.7, 49.3, 49.3, 38.4, 42.8, 49.4, 47.5, 24.4, 31.2, 38.4, 27.4, 33.4, 16.3, 28.3, 25.7, 55.0 and 62.3 (in $10^{-6}\,s^{-1}$) in ethanol, *n*-butanol, *t*-butanol, propane-1,2-diol, 2-butoxyethanol, ethyl methyl ketone, acetic acid, dimethylformamide, acetonitrile, ethyl acetate, 1,4-dioxane, benzene, toluene, chlorobenzene, nitrobenzene, *n*-hexane, chloroform and carbon tetrachloride, respectively ($[PhNH_2] = 0.113\,M$, TiO_2 suspended = 1.0 g, airflow rate = $7.8\,mL\,s^{-1}$, $\lambda = 365\,nm$, $I_0 = 2.46 \times 10^{-5}$ einstein $L^{-1}\,s^{-1}$, volume of reaction solution = 25 mL). The corresponding relative slopes of solar photocatalysis are 1.00, 1.14, 0.76, 1.86, 1.74, 1.62, 1.17, 1.20, 0.62, 1.06, 1.65, 0.41, 0.73, 0.40, 0.29, 0.40, 1.23 and 2.23 ($[PhNH_2] = 0.113\,M$, $TiO_2 = 1.0\,g$, catalyst bed = $12.5\,cm^2$, airflow rate = $4.75\,mL\,s^{-1}$, volume of reaction solution = 25 mL). Calculation of the photocatalytic oxidation rates in different solvents requires the molar extinction coefficients of *cis*- and *trans*- azobenzenes at appropriate wavelengths and the ratio at which *cis*- and *trans*- azobenzenes are formed in each solvent and hence could not be made. The relative slopes of solar photocatalysis do not conform to those with UV light, as they are not the true rates.

4. Conclusions

Although aniline at ppm level is mineralized by illuminated TiO_2, at high concentration it is oxidized to azobenzene. The effects of [aniline], airflow rate, solvent, electron donors, etc. on the rates of solar photocatalyzed oxidation of aniline on TiO_2 are similar to those with UV light. Increase of the surface area of the catalyst bed enhances the solar photocatalysis and makes it comparable with that using UV light, carried out in a continuously stirred tank reactor.

References

[1] Md.K. Nazeeruddin, P. Pechy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, Le Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Gratzel, J. Am. Chem. Soc. 123 (2001) 1613.

[2] Md.K. Nazeeruddin, R. Humphry-Baker, P. Liska, M. Gratzel, J. Phys. Chem. B 107 (2003) 8981.

[3] J.P. Wilcoxon, J. Phys. Chem. B 104 (2000) 7334.

[4] C. Srinivasan, Curr. Sci. 76 (1999) 534.

[5] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1.

[6] C. Srinivasan, N. Somasundaram, Curr. Sci. 85 (2003) 1431.

[7] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.

[8] U. Diebold, Surf. Sci. Rep. 48 (2003) 53.

[9] V. Brezova, A. Blazkova, L. Karpinsky, J. Groskova, B. Havlinova, V. Jorik, M. Ceppan, J. Photochem. Photobiol. A 109 (1997) 177.

[10] S.M. Zakeeruddin, Md.K. Nazeeruddin, R. Humphry-Baker, P. Pechy, P. Quagliotto, C. Barolo, G. Viscardi, M. Gratzel, Langmuir 18 (2002) 952.

[11] V. Iliev, D. Tomova, L. Bilyarska, L. Pirahov, L. Petrov, J. Photochem. Photobiol. A 159 (2003) 281.

[12] G. Alhakimi, L.H. Studnicki, M. Al-Ghazali, J. Photochem. Photobiol. A 154 (2003) 219.

[13] C. Karapire, H. Kolancilar, U. Oyman, S. Icli, J. Photochem. Photobiol. A 153 (2002) 173.

[14] B. Dindar, S. Icli, J. Photochem. Photobiol. A 140 (2001) 263.

[15] M. Santhanam, V. Ramakrishnan, Indian J. Chem. 6 (1968) 88;
M. Santhanam, V. Ramakrishnan, Indian J. Chem. 10 (1972) 927.

[16] R.S. Davidson, P.F. Lambeth, M. Santhanam, J. Chem. Soc., Perkin Trans. 2 (1972) 2351.

[17] M.A. Hema, V. Ramakrishnan, J.C. Kuriacose, Indian J. Chem. 15B (1977) 947.

[18] H. Kasturirangan, V. Ramakrishnan, J.C. Kuriacose, J. Catal. 69 (1981) 216;
H. Kasturirangan, V. Ramakrishnan, J.C. Kuriacose, Indian J. Technol. 19 (1981) 327.

[19] L. Wenhua, L. Hong, C. Sao’an, Z. Jianqing, C. Chunan, J. Photochem. Photobiol. A 131 (2000) 125.

[20] M.A. Fox, M.T. Dulay, Chem. Rev. 341 (1993) 341.

[21] B.R. Mű̋ller, S. Majoni, R. Memming, D. Meissner, J. Phys. Chem. B 101 (1997) 2501.

[22] K. Iseda, A. Towata, E. Watanabe, M. Fukaya, H. Taova, Bull. Chem. Soc. Jpn. 71 (1998) 1249.

[23] C. Karunakaran, S. Senthilvelan, S. Karuthapandian, K. Balaraman, Catal. Commun. 5 (2004) 283.

[24] L. Vincze, T.J. Kemp, J. Photochem. Photobiol. A 87 (1995) 257.