

Photocatalytic bleaching of *p*-nitrosodimethylaniline in TiO₂ aqueous suspensions: A kinetic treatment involving some primary events photoinduced on the particle surface

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Abstract

The photocatalytic bleaching of *p*-nitrosodimethylaniline (P) has been investigated in aqueous suspensions of TiO₂. It was found that both charge carriers (hole and electron) were reactive to P to result in a bleaching. The roles of O₂ and several hole scavengers (HCOO⁻, EDTA, I⁻) have also been examined. A reaction mechanism has been proposed with consideration of several primary processes photoinduced on TiO₂ surface. The results of the kinetic analysis fit fairly well to those of the experiments. The rate constant (k_p^h) of the reaction between P and the adsorbed hydroxyl radical was estimated to be in the order 10¹⁰ M⁻¹ s⁻¹, which is in good agreement with that obtained from the homogeneous reaction of P with free OH[·] radicals. Of particular interest is the pH dependence of the photobleaching rate. Around both p*K*_a of P and pH_{ZPC} of TiO₂, the photobleaching of P was steeply enhanced. This can be reasonably attributed to the mutual interaction (repulsion versus attraction) between P and TiO₂ particles in different pH ranges.

Keywords: Photobleaching; *p*-nitrosodimethylaniline; Titanium dioxide; Photocatalysis

1. Introduction

Photoinduced redox reactions in TiO₂ aqueous suspensions have gained wide interest because of their promising application to solar energy conversion [1] and purification of waste

waters [2]. To improve the catalytic activity of TiO₂ material, many research groups have focused their attention on the mechanistic details of the photoinduced processes. As indicated in some excellent reports and review articles [3–7], the chemical nature of the photogenerated charge carriers (holes and electrons), together with the roles these species played in heterogeneous reactions at TiO₂/solution interface is not revealed yet.

Studying the reaction kinetics of electrons or holes is generally helpful for postulating a reac-

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tion mechanism and can also enhance the understanding of the photocatalytic reaction. However, in previous papers about semiconductor photocatalysis, most of the researchers have paid almost all their attention to either the reduction caused by conduction band electrons [8–10], or the oxidation with the involvement of valence band holes [11–13]. This is possibly due to the difficulty of choosing a species which is reactive to both the two charge carriers. At this point, the finding of a probe which is not only reducible to the conduction band electron but also oxidizable to the valence band hole, will be very significant to probe the kinetics of the photocatalytic redox reactions (especially the primary processes) occurring at the particle interface.

In the present study, we report for the first time the possibility of using *p*-nitrosodimethylaniline (P) as a probe to investigate the kinetic mechanism of the primary redox reactions photoinduced at the TiO₂ particle surface. Extensive investigations by radiolysis [14–16] and photolysis [17–19] have already approved the high efficiency of bleaching P by reacting with both the OH· radical and the hydrated electron, and it has also shown a good selectivity, i.e. neither O₂^{·-} nor singlet oxygen can react with P. So it is possible that similar reactions can occur in the irradiated TiO₂ suspension, for which is believed to be able to produce several reactive species, such as OH·, h⁺ and e⁻. Owing to the large extinction coefficients of P at its maximums (3.4 × 10⁴ M⁻¹ cm⁻¹ at 440 nm for its free form, 2.1 × 10⁴ M⁻¹ cm⁻¹ at 350 nm for the protonated form) [16], it is possible to measure accurately very small changes in concentration just by spectrophotometry.

2. Experimental

2.1. Materials

p-Nitrosodimethylaniline (P), disodium ethylenediaminetetraacetate (EDTA), HCOONa, KI

and AgNO₃ were of laboratory reagent grade and were used without further purification. The TiO₂ powder (P-25, Degussa AG) consists mainly of anatase with a surface area of 55 m²/g and an average diameter of 30 nm. Deionized and doubly distilled water was used throughout this study.

2.2. Methods and apparatus

All irradiation were carried out with a 100 W Hg lamp (λ > 330 nm, Toshiba SHLS – 1002A). To prevent the direct excitation of P, a filter solution of P (10⁻⁴ M) was introduced between the irradiation source and the photo-reaction vessel and thus only the 369 nm light in the irradiation output from the Hg lamp used was available to cause a band-gap excitation of TiO₂. At this wavelength, P has little absorption. As will be seen below, P is quite stable to visible and near UV light in the absence of TiO₂ powder, therefore allowing it to be used as a suitable filter.

In typical experiments, 50 ml of a TiO₂ suspension (0.3 g l⁻¹) containing P (5 × 10⁻⁵ M) and other additives (if necessary), such as HCOO⁻, I⁻ and EDTA, was contained in a 70 ml Pyrex glass vessel. Before illumination, the suspension was magnetically stirred or sonicated for 10 min to ensure that the adsorption process of additives becomes complete on the TiO₂ surface. (Due to the high concentration (0.01 or 0.1 M) of the added ions, the adsorption equilibrium should be reached quite fast.)

During a run, ca. 3.5 ml samples were taken at given time intervals. The samples were then subjected to centrifugation and subsequent filtration by a Millipore membrane (pore size 0.22 μm). The filtrates were analyzed on a Shimadzu 1600 A spectrophotometer. For the reactions in different pH media, the initial pH of the suspension was adjusted by adding HCl or NaOH solution. In the case of studying the photocatalysis under anaerobic condition, the solution was de-aerated with bubbling N₂ gas for at least 10

min before irradiation and continuous N₂ gas purge was employed during the subsequent irradiation.

3. Results and discussion

3.1. Reaction mechanism

Table 1 presents a sequence of all the possible elementary steps that can describe the primary events photoinduced in aqueous TiO₂ suspensions which contain P and hole scavenger, either under air or nitrogen saturated conditions. The purpose of this scheme is to reasonably depict the photoreaction processes of P while making it simple to treat the following kinetic problems.

Eqs. (1)–(3) represent the photogeneration and the subsequent trapping of conduction band electrons (e_{CB}^-) and valence band holes (h_{VB}^+). Eq. (4) describes the recombination process of the two charge carriers. Considering the weak intensity of the steady-state irradiation used in this study, the average charge carrier number formed in one TiO₂ particle must be small enough [20], so that most of the charge carriers are rapidly trapped at particle surface. In such a case, the rate of the recombination between trapped electrons and trapped holes is determined by the diffusion of the holes away from their trap sites [4,21].

The reduction potential of P is +0.04 V versus NHE at pH 7.0 as measured by a cyclic voltameter. This makes it possible for P to accept an trapped electron (located below the conduction band of TiO₂, -0.7 V versus NHE for anatase at pH 7.0 [6]) to cause a reductive bleaching (Eq. 5). An alternative bleaching pathway for P is to be oxidized by trapped holes (Eq. 6). This is doubtless possible because that the positive potential of the valence band of TiO₂ (+2.5 V versus NHE at pH 7.0) is much higher than the oxidation potential of P (only

+0.3 V versus NHE at pH 7.0). Fig. 1 shows a photobleaching of P in a typical case, an air-saturated solution (50 ml) containing 5.0×10^{-5} M P and 0.3 g l^{-1} TiO₂ at pH 5.5. Upon irradiation with the light ($\lambda \sim 369 \text{ nm}$), the absorption band at 440 nm (i.e. λ_{max} of the unprotonated form of P) disappeared steadily accompanied by an increase in absorption at 200–250 nm. Control experiments showed that the presence of TiO₂ was necessary to cause the photobleaching, otherwise, no bleaching was observed. The increase in absorption at the shorter wavelength was attributed to the additive products by hydroxyl radicals and hydrated electrons [16,19]. No degradation (cleavage of the benzene ring) of P was observed within the photobleaching process.

Note that the subsequent reactions of the primary products (P^{•-} or PH[•] and POH[•]) are complicated and tedious to list [14]. Thinking of the fact that the purpose of this study is to investigate the primary photobleaching kinetics of P, we do not refer to the subsequent reactions further.

To investigate the nature of reaction kinetics, some reducing agents were used as hole scavengers to compete with P for hole oxidation. For this purpose two categories of scavengers were chosen, one is the oxidized product (S⁺) of the trapped hole (Eq. 7), a strongly reducing specie, which can readily cause a reductive bleaching of P (Eq. 8), whereas the other is the oxidized product from Eq. (7), which is not reactive to P but undergoes irreversible dimerization or decomposition. One candidate chosen for the former use is HCOO⁻, which is verified to be an efficient OH[•] scavenger to generate COO⁻, a good electron donor for the reduction of P [14]. Two anions, I⁻ and EDTA, were used as another kind of hole scavengers. The oxidized product of I⁻, I[•], dimerizes rapidly to form I₂ (actually I₃⁻ in aqueous solution, formed by binding an I⁻ ion), while the oxidized EDTA undergoes a facile, irreversible decomposition to produce glyoxylic acid and ethylenediamine-*N,N'*-diacetic acid [22]. In this study, we will

examine the different roles played by the two kinds of hole scavengers through a critical kinetic analysis. The specific role of O_2 will also be considered in our study when formulating the kinetic rate laws (Eqs. 9 and 10).

3.2. Kinetic analysis

Of particular interest to the kinetic treatment of heterogeneous catalysis is the *surface concentration* of reactants, which can be related to

Table 1
Possible primary reactions photoinduced on TiO_2 surface

Primary processes	Reaction rates
$TiO_2 \xrightarrow{h\nu} h\nu_{VB}^+ + e_{CB}^- \quad I$	(1) ^a
$e_{CB}^- + \{-Ti^{IV}-\}_{surf} \rightarrow \{-Ti^{III}-\}_{surf}$	very fast, picoseconds (2) ^b
$h\nu_{VB}^+ + \{Ti^{IV}-O^{2-}-Ti^{IV}-\}_{subsurface}-OH^- \rightarrow \{Ti^{IV}-O^{\cdot-}-Ti^{IV}-\}-OH^- \leftrightarrow \{Ti^{IV}-O^{2-}-Ti^{IV}-\}-OH^{\cdot}$	fast, nanoseconds (3) ^b
$h_{tr}^+ + e_{tr}^- \rightarrow \text{heat}$	$k_{tr} [h_{tr}^+]$ (4)
$e_{tr}^- + P \xrightarrow{H^+} P^{\cdot-} \text{ or } PH^{\cdot}$	$k_p^e [P][e_{tr}^-]$ (5)
$h_{tr}^+ + P \xrightarrow{OH^-} POH^{\cdot}$	$k_p^h [P][h_{tr}^+]$ (6)
$h_{tr}^+ + S \rightarrow S^{\cdot+}$	$k_s^h [S][h_{tr}^+]$ (7) ^c
$S^{\cdot+} + P \xrightarrow{H^+} S^{2+} + P^{\cdot-} \text{ or } PH$	$k_p^s [P][S^{\cdot+}]$ (8)
$e_{tr}^- + O_2 \rightarrow O_2^{\cdot-}$	$k_o^e [O_2][e_{tr}^-]$ (9)
$S^{\cdot+} + O_2 \rightarrow O_2^{\cdot-} + S^{2+}$	$k_o^s [O_2][S^{\cdot+}]$ (10)

^a I is the rate of photon absorption by TiO_2 particles.

^b $\{-Ti^{III}-\}_{surf}$, $\{Ti^{IV}-O^{\cdot-}-Ti^{IV}-\}-OH^- \leftrightarrow \{Ti^{IV}-O^{2-}-Ti^{IV}-\}-OH^{\cdot}$ are abbreviated as e_{tr}^- , h_{tr}^+ respectively for convenience.

^c S represents the hole scavenger (e.g. $HCOO^-$, EDTA and I^-) employed in this study.

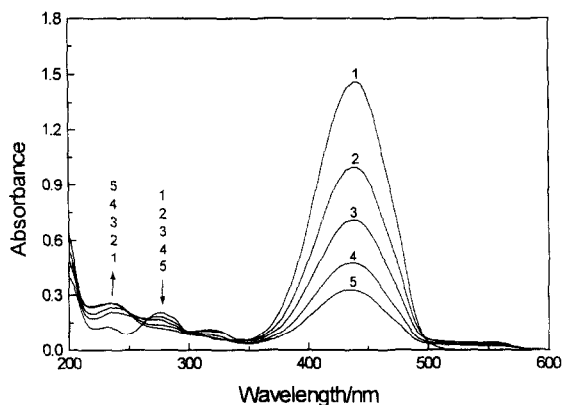


Fig. 1. Absorption spectra showing the photobleaching of P when irradiated in aqueous TiO_2 suspensions under air-saturated condition: TiO_2 0.3 g l^{-1} , P $5.0 \times 10^{-5} \text{ M}$, pH 5.5, $\lambda \sim 369 \text{ nm}$. The irradiation times were: (1) 0, (2) 4, (3) 8, (4) 14 and (5) 18 min.

the bulk concentration through a Langmuir isotherm. In this study, we recognize two extreme situations in simplifying the Langmuir isotherm for P and the hole scavengers. (1) Despite continuous effort, it is proved that the determination of the adsorption isotherm of P on TiO_2 is very difficult. Even in strong basic media where the adsorption of P is favored, only a few percent was adsorbed, ca. 4% at $1.2 \text{ g l}^{-1} \text{ TiO}_2$, $2.0 \times 10^{-5} \text{ M P}$ and pH 11; whereas in acid media (pH 1.8) no detectable adsorption of P was found. Maybe this is due to the lack of strong adsorbing group (e.g. $-\text{COO}^-$) in P. Consequently, it is reasonable to simplify the Langmuir isotherm as

$$[\text{P}]_{\text{surf}} = K_{\text{app}}[\text{P}] \quad (11)$$

here the apparent adsorption coefficient K_{app} relates directly to the surface and bulk concentrations of P. In the rate equations for reactions of P in Table 1, the bulk concentration of P is used directly and the apparent adsorption coefficient K_{app} is considered respectively in the rate constant. It should be emphasized here that although P is only adsorbed to a slight extent on TiO_2 particles, the extent of *photoadsorption* is unknown [23]. (2) Regarding another extreme situation that various hole scavengers (HCOO^- , EDTA and I^-) with much higher concentrations (0.01 or 0.1 M) compared with that of P ($5.0 \times$

10^{-5} M) were used, we assume that the concentration of these scavengers remains essentially constant during the photobleaching of P and so that the surface concentration of the scavenger, which is in equilibrium with the bulk concentration, is approximately unchanged. In such a case, the constant surface concentration $[\text{S}]_{\text{surf}}$ can be expressed as the bulk (i.e. initial) concentration $[\text{S}]$ by multiplied by ratio K' ,

$$[\text{S}]_{\text{surf}} = K'[\text{S}] \quad (12)$$

Again in Table 1 the concentration term $[\text{S}]$ used in all rate equations refers to the bulk (initial) concentration of the hole scavenger used, and also the ratio K' is included in each of the rate constants. The two assumptions made above were proved extremely useful for deriving the steady-state equations below, also because of the assumptions, experimental results here fit excellently to those of the kinetic analysis.

Under continuous illumination, the rate of photobleaching of P will be given by

$$-\frac{d[\text{P}]}{dt} = k_{\text{p}}^{\text{c}}[\text{P}][e_{\text{tr}}] + k_{\text{p}}^{\text{h}}[\text{P}][h_{\text{tr}}^+] + k_{\text{p}}^{\text{s}}[\text{P}][\text{S}^+] \quad (13)$$

The concentrations of the trapped charge carriers (h_{tr}^+ and e_{tr}^-) and the oxidized hole scavenger (S^+) should satisfy the steady-state approximation, then

$$\frac{d[e_{\text{tr}}^-]}{dt} = 0, \quad \frac{d[h_{\text{tr}}^+]}{dt} = 0, \quad \frac{d[\text{S}^+]}{dt} = 0$$

From these we get

$$[h_{\text{tr}}^+] = \frac{I}{k_{\text{tr}} + k_{\text{p}}^{\text{h}}[\text{P}] + k_{\text{s}}^{\text{h}}[\text{S}]} \quad (14)$$

$$[e_{\text{tr}}^-] = \frac{I}{k_{\text{tr}} + k_{\text{p}}^{\text{h}}[\text{P}] + k_{\text{s}}^{\text{h}}[\text{S}]} \left[\frac{k_{\text{p}}^{\text{h}}[\text{P}] + k_{\text{s}}^{\text{h}}[\text{S}]}{k_{\text{p}}^{\text{e}}[\text{P}] + k_{\text{o}}^{\text{e}}[\text{S}]} \right] \quad (15)$$

$$[\text{S}^+] = \frac{I}{k_{\text{tr}} + k_{\text{p}}^{\text{h}}[\text{P}] + k_{\text{s}}^{\text{h}}[\text{S}]} \left[\frac{k_{\text{s}}^{\text{h}}[\text{S}]}{k_{\text{p}}^{\text{s}}[\text{P}] + k_{\text{o}}^{\text{s}}[\text{S}]} \right] \quad (16)$$

From Eqs. (13)–(16), we can get the Eq. (17),

$$-\frac{d[P]}{dt} = \frac{I}{k_{tr} + k_s^h[S] + k_p^h[P]} \times \left(k_p^h[P] + \frac{k_s^h[S]}{1 + k_o^s[O_2]/k_p^s[P]} + \frac{k_s^h[S] + k_p^h[P]}{1 + k_o^e[O_2]/k_p^e[P]} \right) \quad (17)$$

This represents actually the most complex case where a TiO_2 suspension containing P and $HCOO^-$ is irradiated under aerobic condition. Eq. (17) was tested extensively in a series of steady-state irradiation under various relatively simple conditions. The results of this work are as follows.

3.2.1. $HCOO^-$ as scavenger in anaerobic condition (i.e. O_2 -free)

In such a case, the O_2 -containing term in Eq. (17) is removed. If an assumption is made that $k_p^h[P] \ll k_s^h[S]$, i.e. the capture of the trapped hole by P (Eq. 6) is suppressed by $HCOO^-$ which is at a much higher concentration, Eq. (17) can be simplified as

$$-\frac{d[P]}{dt} = \frac{2Ik_s^h[S]}{k_{tr} + k_s^h[S]} \quad (18)$$

A zero order kinetics is obtained. Integration of Eq. (18) yields

$$[P] = [P]_0 - \frac{2Ik_s^h[S]}{k_{tr} + k_s^h[S]} t \quad (19)$$

Thus a plot of $[P]$ versus irradiation time should give a straight line (as shown in Fig. 2) where the slope equals the apparent zero order rate constant $2Ik_s^h[S]/(k_{tr} + k_s^h[S])$. Fig. 2 also shows the changes in the concentration of P as a function of irradiation time under air-saturated condition. As inferred from Eq. (17), the plot shows a more complex behavior together with a lower initial reaction rate in comparison with the O_2 -free case.

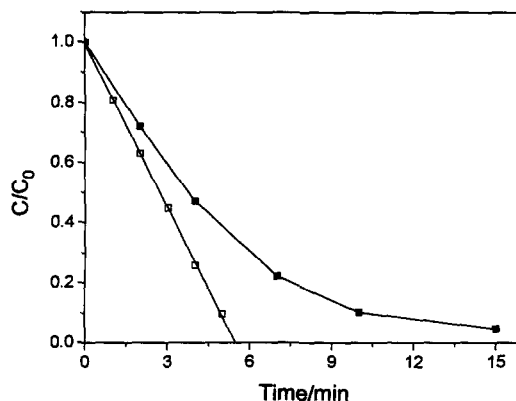


Fig. 2. Plots of the normalized concentration as a function of irradiation time for the photobleaching of P in the presence of 0.1 M $HCOONa$ under air-saturated (■) and N_2 -saturated (□) conditions. The other conditions were the same as in Fig. 1.

3.2.2. EDTA or I^- as scavenger

An essential distinction between the case using EDTA or I^- as the hole scavenger and the one with the employment of $HCOO^-$ is whether reaction (8) in Table 1 exists or not, i.e. the oxidized products of EDTA or I^- by capturing a trapped hole are not reactive enough to P to cause a bleaching. Therefore, the contribution of the two subsequent reactions (Res. 8 and 10) of the hole scavenger should be excluded from Eq. (13). If again assuming that $k_p^h[P] \ll k_s^h[S]$, Eq. (17) reduces to

$$-\frac{d[P]}{dt} = \frac{Ik_s^h[S]}{k_{tr} + k_s^h[S]} \times \frac{1}{1 + k_o^e[O_2]/k_p^e[P]} \quad (20)$$

In the anaerobic condition, Eq. (20) will be further simplified as

$$-\frac{d[P]}{dt} = \frac{Ik_s^h[S]}{k_{tr} + k_s^h[S]} \quad (21)$$

Integration of Eq. (21) gives

$$[P]_0 - [P] = \frac{Ik_s^h[S]}{k_{tr} + k_s^h[S]} t \quad (22)$$

As illustrated in Fig. 3, the photobleaching of P in an anaerobic condition with either EDTA or I^- as hole scavenger really appears to obey a zero order kinetics to a high degree ($\sim 95\%$ for

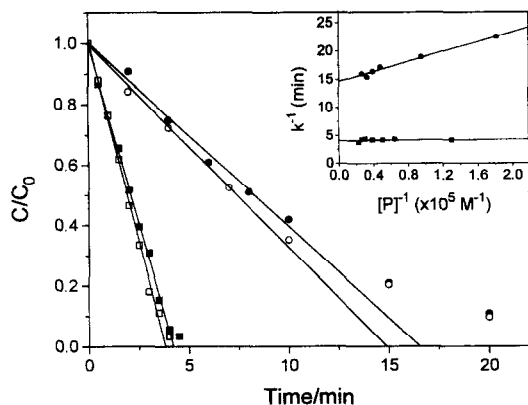


Fig. 3. Plots of the normalized concentration as a function of irradiation time for the photobleaching of P in the presence 0.01 M EDTA or KI under air or N_2 saturated conditions: (●) I^- + air, (○) I^- + N_2 , (■) EDTA + air and (□) EDTA + N_2 . The other conditions were the same as in Fig. 1. The insert depicts plots of k^{-1} versus $[P]^{-1}$ (see main text for explanation).

EDTA) in the reaction as predicted from Eq. (22). It can be seen that the photobleaching rate in the EDTA case is much higher than that of the I^- case. One reason of this is attributed to the much stronger adsorbability of EDTA on TiO_2 , as it has four $-COO^-$ groups which can well bind to the TiO_2 surface, it implicates a much higher k_s^h which includes the adsorption ratio K' (Eq. (12)). Another alternative reason may be the back reaction of I_3^- with the trapped electron. Such a back reaction also leads to a deviation of the plot for I^- from the linearity at the latter stage of the photobleaching (see below).

It is surprising to see that even in an aerobic condition the photobleaching of P also approximates zero order kinetics (for I^- , to an extent of ca. 65% of the reaction), since Eq. (20) predicts a somewhat complex rate dependence on the concentration of P. The only assignment for this discrepancy is that the ratio $k_o^e[O_2]/k_p^e[P]$ in Eq. (20) is very small as will be shown below.

$$1 - \frac{[P]}{[P]_0} = \frac{Ik_s^h[S]}{[P]_0(k_{tr} + k_s^h[S])} \times \frac{1}{1 + k_o^e[O_2]/k_p^e[P]} t \quad (23)$$

If denoting the apparent rate constant as k , Eq. (23) becomes

$$1 - \frac{[P]}{[P]_0} = kt \quad (24)$$

From the experimental results, the k values at different irradiation times can be obtained according to Eq. (24). The reciprocal of k can be expressed as

$$k^{-1} = X + X \cdot \frac{k_o^e[O_2]}{k_p^e} \cdot [P]^{-1} \quad (25)$$

where X equals to $[P]_0(k_{tr} + k_s^h[S])/Ik_s^h[S]$. The insert in Fig. 3 illustrates that as predicted by Eq. (25), a plot of k^{-1} versus $[P]^{-1}$ yields approximately a straight line. From the ratio of slope to intercept, one can obtain the value of $k_o^e[O_2]/k_p^e$, ca. 1.9×10^{-7} M and 3.0×10^{-6} M for the cases of EDTA and I^- respectively. This ensures that during the photobleaching of 5×10^{-5} M P, the quantity of $k_o^e[O_2]/k_p^e[P]$ remains as significantly small (< 1) as assumed earlier. For EDTA, even to the extent of 95% of P consumed, the value of $k_o^e[O_2]/k_p^e[P]$ keeps as low as 0.07. As a result, the reaction with the employment of EDTA obeys zero order kinetics almost until the completeness of the photobleaching (see Fig. 3). In contrast, due to the higher value of $k_o^e[O_2]/k_p^e$, the plot for I^- in Fig. 3 remains the linearity only to a degree of ca. 65% of the photobleaching. The higher value of $k_o^e[O_2]/k_p^e$ for I^- can be attributed to the fact that to a certain extent, part of I_3^- species compete with P in reacting with the trapped electrons (Eq. (26)), especially at the latter stage of the photobleaching when the amount of I_3^- outnumbers that of P.



It seems possible for Eq. (26) to occur because of the favorable redox potential of $E^0(I_3^-/3I^-) = 0.536$ V versus NHE [24] with respect to the conduction band potential of TiO_2 . Coupling Eq. (7) and Eq. (26) forms a short circuit reac-

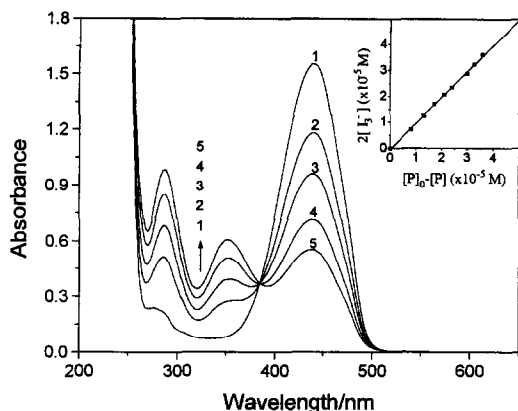


Fig. 4. Absorption spectra showing the photobleaching of P and the photo-formation of I_3^- when irradiated in the TiO_2 suspensions under air-saturated condition: TiO_2 0.3 g l^{-1} , P $5.0 \times 10^{-5} \text{ M}$, KI 0.01 M , pH 5.5, $\lambda \sim 369 \text{ nm}$. The irradiation times were: (1) 0, (2) 4, (3) 8, (4) 14 and (5) 18 min. The insert shows a plot of $2[I_3^-]$ versus $[P]_0 - [P]$, where $[P]_0$ is the initial concentration of P.

tion for I^- , thus can provide an alternative pathway for the indirect recombination of electron-hole pairs. The overall effects are that the apparent rate constant k_o^e for O_2 to scavenge an electron (Eq. 9) will increase, for simplification, Eq. (26) is not considered in the reaction mechanism (Table 1).

Due to the strong extinction of I_3^- at 353 nm ($\epsilon = 2.64 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 287.5 nm ($\epsilon = 4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [25], it is possible to investigate the oxidation of I^- accompanying the photobleaching of P. Fig. 4 presents the spectral changes as a function of irradiation time for a TiO_2 suspension containing $5.0 \times 10^{-5} \text{ M}$ P and 0.01 M KI. The spectral features are in sharp contrast with that shown in Fig. 1. Concomitantly with the disappearance of the absorption band at 440 nm of P, the two absorption bands of I_3^- appear at short wavelengths, indicating the occurrence of the oxidation of I^- by the trapped hole (Eq. 7). The development of a clear isobestic point at 380 nm implicates a quantitative balance between the disappearance of P and the formation of I_3^- , i.e. for every two trapped holes being scavenged by two I^- ions

to generate one I_3^- ion, two P molecules are consumed by reacting with the two trapped electrons left at the TiO_2 surface. This is further confirmed in the insert in Fig. 4, where a plot of $2[I_3^-]$ versus $[P]_0 - [P]$ produces a straight line with a slope of unity. Control experiments showed that in the absence of TiO_2 , no I_3^- could be formed under the same irradiation condition. These results strongly rationalized the two assumptions that $k_p^h[P] \ll k_s^h[S]$ and $k_o^e[O_2] \ll k_p^e[P]$ made above, i.e. either EDTA or I^- plays the dominant role to scavenge the trapped hole, while P scavenges the left electron in effective competition with O_2 .

Considering the fact that unlike I_3^- , the oxidized product of EDTA has little interference in the reaction kinetics, in the following we use the value $1.9 \times 10^{-7} \text{ M}$ of $k_o^e[O_2]/k_p^e$ derived from the EDTA case to estimate the rate constant. From the results of Brown et al. [8] who investigated extensively the photoreduction of methyl orange sensitized by colloidal TiO_2 , we deduce the rate constant k_o^e to be $1.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH5.5 and together with the equilibrium concentration of O_2 in air-saturated water $2.0 \times 10^{-4} \text{ M}$, we can obtain a value for k_p^e $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is about 25 times lower than that obtained from the homogeneous radiolysis of P [14], in which the rate constant of the reaction between P and the hydrated electron was found to be $3.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The lower rate constant infers a less reactivity of the trapped electron compared with the free one. Also, control experiments show that without TiO_2 , no photobleaching of P in the presence of EDTA could be observed.

3.2.3. No hole scavenger

To test further the reliability of Eq. (17) and to investigate the effects of the addition of hole scavenger on the kinetics of photobleaching of P, some control experiments have been undertaken without addition of hole scavengers under N_2 -saturated conditions. In such cases, all the terms including hole scavengers and O_2 are

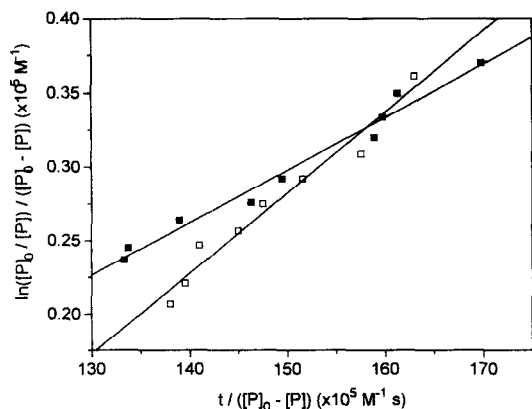


Fig. 5. Plots of $\ln([P]_0/[P]) / ([P]_0 - [P])$ versus $t / ([P]_0 - [P])$ (see main text). Data are from the photobleaching of P (5.0×10^{-5} M) under N_2 -saturated condition in the TiO_2 suspension (0.3 g l^{-1} , $\lambda \sim 369 \text{ nm}$) at different pH: (■) 9.0 and (□) 5.6.

eliminated from Eq. (17), which is thus simplified to

$$-\frac{d[P]}{dt} = \frac{2Ik_p^h[P]}{k_{tr} + k_p^h[P]} \quad (27)$$

Integration of Eq. (27) gives

$$\frac{\ln([P]_0/[P])}{[P]_0 - [P]} = -\frac{k_p^h}{k_{tr}} + \frac{2Ik_p^h}{k_{tr}} \times \frac{t}{[P]_0 - [P]} \quad (28)$$

A plot of $\ln([P]_0/[P]) / ([P]_0 - [P])$ versus $t / ([P]_0 - [P])$ should be linear as predicted from Eq. (28). Fig. 5 shows the results of the photobleaching of P at different pH under a N_2 -saturated condition. A linear regression produces the intercept, i.e. the ratio of $-k_p^h/k_{tr}$, to be -5.1×10^4 and $-2.4 \times 10^4 \text{ M}^{-1}$ for pH 5.6 and pH 9.0 respectively. Thus, using the k_{tr} value of $5.5 \times 10^5 \text{ s}^{-1}$ deduced from the results of Rothenberg et al. [21], we can estimate k_p^h at both pH to be 2.8×10^{10} and $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which is in surprising agreement with that obtained from the homogeneous radiolysis and photolysis study [14,16], where the determined rate constant for the reaction of free OH^\cdot with P at pH 9.0 was also in the range $1\text{--}1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The good agreement implicates that

the trapped hole depicted in Table 1 has quite the same chemical nature (at least the oxidizing power) as the free OH^\cdot radical.

The two forms of the trapped hole ($\{Ti^{IV}-O^\cdot-Ti^{IV}\}-OH^-$ and $\{Ti^{IV}-O^{2-}-Ti^{IV}\}-OH^\cdot$) depicted in Eq. (3) are in a rapid resonance equilibrium. Due to the stabilization by the resonance with the subsurface oxygen, there is some bond character between the adsorbed OH^\cdot radical and Ti^{IV} ion on TiO_2 surface. That is, there is little possibility for these OH^\cdot radicals to migrate far from the TiO_2 surface and in order to react with OH^\cdot the reactant must be preadsorbed or attracted toward the surface of TiO_2 particles. The adsorption on TiO_2 depends to a great extent on the surface charge, which in turn varies as a function of pH of the solution. The pH effect on the kinetics of photobleaching of P will be discussed in the following section.

3.3. pH effect

Since pH often affects notably the reaction kinetics of the heterogeneous photocatalysis, the photobleaching of P was investigated at various pH in the present study as shown in Fig. 6. Clearly, increases of pH always favor the reaction. This is attributed to the two types of acid–base equilibrium present in the reaction

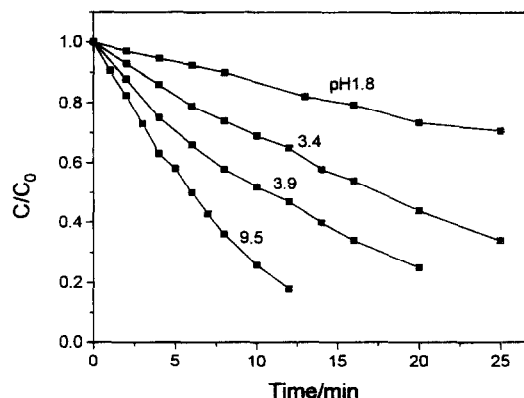
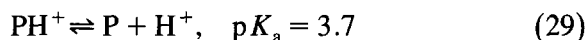


Fig. 6. Plots of the normalized concentration as a function of irradiation time for the photobleaching of P under the same conditions as in Fig. 1 but at different pH as denoted in the figure.

solution, one exists between the surface groups on TiO_2 and the other between the free and protonated form of P (Eq. (29)) [16].



For the P-25 TiO_2 powder used in this study, the zero point of charge (pH_{zpc}) for the surface was determined by Zhao et al. [26], to be at pH 6.8. When $\text{pH} > \text{pH}_{\text{zpc}}$, the particle surface will be negatively charged, while when $\text{pH} < \text{pH}_{\text{zpc}}$ a positive charge will be formed on the TiO_2 surface. Considering the $\text{p}K_a$ of P, we can expect three pH ranges by dividing the whole pH range in the interaction between P and TiO_2 particles, (i) $\text{pH} < 3.7$, the positively charged TiO_2 particle repulses strongly the P molecule which also possesses a positive charge and thereby negligible adsorption of P occurs on the TiO_2 surface; (ii) $3.7 < \text{pH} < 6.8$, repulsion between the free form of P and the less positive surface of TiO_2 is weaker compared with the first case and (iii) $\text{pH} > 6.8$, the TiO_2 surface now becomes negatively charged and the attraction between TiO_2 particle and P is thus enhanced. From these discussions, a pH dependence of the initial rate of photobleaching of P will be anticipated as depicted in Fig. 7. Within the whole pH range tested, there are two pH points around which the initial rate increases more steeply. This can be clearly recognized in

the first derivative plot also shown in Fig. 7. It is noteworthy that the two pH points correspond to the $\text{p}K_a$ 3.7 of P and the pH_{zpc} 6.8 of the P-25 TiO_2 powder.

In addition to the pH effect on adsorption of P, it is also possible that the pH dependence of the TiO_2 conduction band can also explain the increase in initial rates described in Fig. 7. As reported in previous papers [27,28], the conduction band potential of TiO_2 (E_{CB}) shifts cathodically with pH. A more negative E_{CB} will certainly be useful to increase the reducing power of the conduction band electron, and thus promote the reduction of P (Eq. 5). However, this explanation seems hardly plausible for the results in Fig. 7, since a steady decrease in E_{CB} with pH should result in a simple increase in the reaction rates, but not the plot feature in Fig. 7. On the other hand, in parallel with the decrease in E_{CB} , the valence band edge E_{VB} also decreases by 59 mV for each increasing unit of pH, leading to a weakness in the oxidizing power of the trapped hole (Eq. 6). This passive effect will reasonably offset the enhancement of the reducing power of the trapped electron. Therefore, it seems that surface adsorption of P on TiO_2 particles, rather than shifts in nominal redox potentials of h_{tr}^+ and e_{tr}^- , plays a dominant role in determining the reactivity of photocatalytic bleaching of P.

4. Conclusions

In this study, the kinetics of several primary reactions photoinduced on TiO_2 particles was investigated by the use of a good probe of *p*-nitrosodimethylaniline (P). The results obtained refer to a surface process for the photocatalytic bleaching of P. The rate constant k_p^h for the reaction of P with the trapped hole is estimated from the kinetic analysis, to be $1\text{--}1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, which fits fairly well to that obtained from the homogeneous reaction of P with free OH^\cdot radicals. This implicates that the trapped hole (i.e. adsorbed OH^\cdot radical) at TiO_2

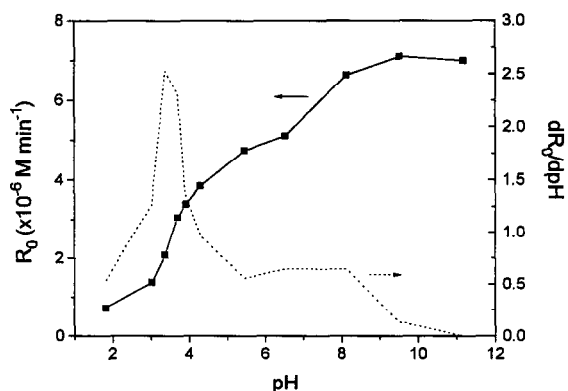


Fig. 7. pH dependence of the initial rate for the photobleaching of P. The dotted line gives the first derivation of the plot.

surface is similar in oxidizing power to the OH[·] radical in solution.

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