

Photooxidation of an azo dye induced by visible light incident on the surface of TiO₂

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Abstract

Oxidation of Acid Orange 7 (AO7) induced by visible light on TiO₂ surfaces has been probed by FT-IR spectroscopy for identification and kinetic studies of degradation products. The tautomerism has been considered for this type of azo dye. The hydrazone form of AO7 triggers and undergoes the photooxidation process initiated by an electron injection into the conduction band of TiO₂. Identification of degradation products by FT-IR spectroscopy reveals the presence of C₂ carboxylic aliphatic acids, carbonates and oxygenated sulfur compounds on TiO₂ surfaces. Kinetics data suggest the existence of several mechanisms and that the photooxidation process is controlled by the supply of molecular oxygen onto the TiO₂ surface. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO₂; Azo dye; Photooxidation; Electron transfer; Visible light

1. Introduction

Textile dyes are of environmental interest, because of their widespread use, their potential to form toxic aromatic amines and their low removal rate during aerobic waste treatment. 700 000 tonnes of dyes are produced in the world and about 50% among them are azo dyes. Estimates indicate that approximately 15% of the synthetic textile dyes used are lost in waste streams during manufacturing or processing operations. These waste waters cannot be treated simply and require expensive methods. Indeed, dyes are designed to have a good fastness under typical usage conditions and, thus, are resistant to microbial attack.

In this paper, we deal with an emergent process using visible light as an alternative solution to eliminate hazardous dyes. This process is inspired by the principle of photosensitization of wide band gap semiconductors. Close attention is paid today to this research field since it is not only important for light conversion into storable energy, but also for all photosensitization mechanisms such as the photographic process or imaging science. To our knowledge, the earlier pioneers who recognized the potential of this process for the remediation of hazardous colored compounds are Kamat et al. [1–3], rapidly followed by Ross et al. [4]. Another research

group has recently examined the mechanism of degradation of several dyes under visible light irradiation [5]. Also the mechanism of photodegradation of an aminoazobenzene dye by three advanced oxidation processes, UV/H₂O₂, UV/TiO₂, and VIS/TiO₂, has been compared [6]. Vinodgopal et al. [7] have studied the photodegradation of AO7 by the photosensitization pathway. These authors have followed the kinetics of the dye disappearance by UV–VIS spectroscopy. They have identified benzene sulfonate and phthalic acid as the final degradation products, but their formation kinetics were not studied. Aromatic *o*-hydroxy azo compounds, such as AO7, undergo a very fast intramolecular proton transfer which leads to a tautomerism. In the present paper, the tautomerism aspect of this kind of dyes has been considered. Very recently, we have shown that AO7 dye adsorbed onto the TiO₂ surface exists in its the hydrazone form [8]. Here, the kinetic of appearance of the degradation products has been probed by transmission FT-IR spectroscopy and a thorough attribution of the bands for the final FT-IR spectra showed that the final degradation products are aliphatic acids and carbonates. Finally, the kinetics data gave some highlights about the mechanism.

2. Experimental section

AO7 was obtained from Aldrich; it is salt free and HPLC pure. TiO₂ P25 (80% anatase, 20% rutile) came from Degussa AG with an elementary particle size of 30 nm and

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a BET specific surface area of $50 \text{ m}^2 \text{ g}^{-1}$. All experiments were carried out at room temperature with doubly distilled water. The irradiation source used is a HeCd monochrome laser ($\lambda = 442 \text{ nm}$) with an optical output power of 80 mW .

The experiments with aqueous suspensions of TiO_2 (5 g l^{-1}) were carried out in a 1 cm thick cell containing $40 \mu\text{mol l}^{-1}$ of AO7 with a pH of 4.8. The colored suspensions were magnetically stirred in the dark for 30 min to reach the adsorption equilibrium. During irradiation, agitation was maintained to keep the suspension homogeneous. The suspension was irradiated under air-equilibrated conditions with visible light laser. Samples were taken to be filtered through a Millipore membrane ($D = 450 \text{ nm}$). Electronic absorption spectra of the aqueous solutions were performed on Perkin-Elmer 554 spectrophotometer.

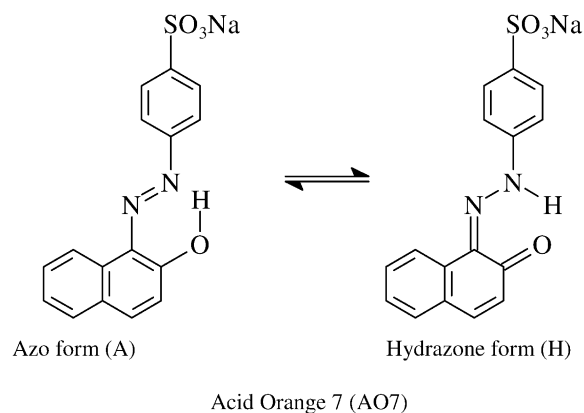
AO7– TiO_2 complexes were prepared by mixing a suspension of 100 ml of TiO_2 (10 g l^{-1}) which contained $10^{-5} \text{ mol l}^{-1}$ of AO7 at $\text{pH} = 4.5$ for 1 h. The colored powders were separated by filtration on a Millipore membrane ($D = 450 \text{ nm}$). The AO7 concentration in the aqueous phase was determined by UV–VIS. spectrophotometry at $\lambda_{\text{max}} = 485 \text{ nm}$. The dye coverage calculated by solving the mass balance of the system for TiO_2 was $4 \times 10^{-7} \text{ mol g}^{-1}$. Then, the samples were dried at 60°C under air ventilation in the dark.

Thin AO7– TiO_2 complex wafers were performed by compressing 20 mg of pure AO7– TiO_2 . The pellets were held perpendicular to the incident visible light beam on a Spectra Tech stand. FT-IR spectra were recorded, after different times of exposure to the visible light beam, on a Perkin-Elmer 1600 spectrophotometer by averaging 30 scans at an instrument resolution of 4 cm^{-1} . Contributions of FT-IR bands of TiO_2 were subtracted before noting the absorbance data of the characteristic bands of AO7 and of the degradation products. By the Beer–Lambert law, direct quantitative information was obtained for the surface concentration of the species. Since, the thickness of the sample remains the same during analysis, the intensity of the bands are proportional to the concentrations of the surface species which disappear or appear; all band intensities are in the range where the Beer–Lambert law can be applied.

AO7– TiO_2 powders were not diluted with KBr to avoid a decrease of the absorbance of the bands of the adsorbed species. The area of spectral information was restricted to the range $1000\text{--}1900 \text{ cm}^{-1}$ because of the strong absorbance of TiO_2 under 1000 cm^{-1} . This area is the region where the molecules put their fingerprints.

3. Results

The use of a monochromatic visible beam ($\lambda = 442 \text{ nm}$) permits to excite selectively the molecular adsorbate AO7 since the photon energy of the laser (2.8 eV) does not allow the activation of the semiconductor TiO_2 which requires a photon with an energy greater than 3.1 eV .



3.1. Degradation in an aqueous suspension of TiO_2

AO7 was chosen, because this dye is a good example of the large family of the phenylazonaphthol dyes. The hydrox-yazodyes undergo azo-hydrazone tautomerism. The hydrazone form is bathochromic compared with the azo form and has usually a higher tinctorial strength. Very recently, the TiO_2 -photocatalyzed degradation of AO7 has been reported, but the tautomerism was not considered [9]. Whereas, it was observed that the hydrazone form is more stable, when the dye is adsorbed onto the TiO_2 surface [8]. The electronic absorption spectrum of AO7 is presented in Fig. 1. The spectrum of AO7 in the visible region exhibits a main band with a maximum at 485 nm and a shoulder at 430 nm . In aqueous phase, the two forms of AO7 are in equilibrium; the band at 485 nm reveals the presence of the hydrazone form, whereas the shoulder at 430 nm indicates the presence of the azo form. Fig. 1 shows the electronic absorption change of AO7 after 3 h of irradiation with visible light in a TiO_2 aqueous suspension. The total disappearance of the band at 485 nm reveals that AO7 is completely eliminated in the TiO_2 aqueous suspension. It should be noted that in the UV region,

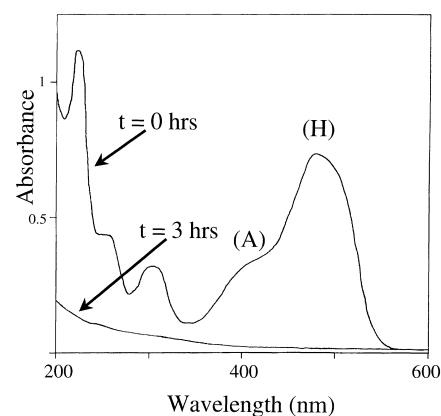


Fig. 1. Electronic absorption spectra of the aqueous solution of AO7 at $t = 0 \text{ h}$ and after 3 h of irradiation with visible light beam ($\lambda = 442 \text{ nm}$). $C_{\text{AO7}} = 4 \times 10^{-5} \text{ M}$, (TiO_2 , 5 g l^{-1}) $\text{pH} = 4.8$. H and A show the electronic absorption bands linked to the hydrazone and the azo tautomer, respectively.

the absorbance is also strongly reduced. For example, at 254 nm, the optical density decreases about 80%. In parallel, the same experiments were undertaken without TiO₂. After 3 h of irradiation, no degradation of the dye was observed. In the dark and in the presence of TiO₂, no reaction occurs.

Since the photochemical oxidative events occur on the TiO₂ surface, we studied the photooxidation in a gas/solid system. In a precedent study [8], it was shown that in aqueous suspension of TiO₂, two kinds of population of AO7 exist when the system is at equilibrium: (i) free AO7 molecules in the aqueous phase; (ii) AO7 molecules anchored on the TiO₂ surface.

3.2. Degradation in a gas/solid system

The electronic absorption spectra of TiO₂ powder and of AO7 adsorbed on TiO₂ are presented in Fig. 2. TiO₂ exhibits no absorption in the visible region. The fundamental absorption edge lies at 400 nm that corresponds to a band gap energy of 3.1 eV. The AO7 maximum absorption is still located at 485 nm as in the aqueous phase. However, a tail in the red up to 600 nm appears, whereas in solution there is no absorption beyond 550 nm. Thus, there is a pronounced broadening of the electronic absorption spectrum of adsorbed AO7 that indicates a strong interaction with the TiO₂ surface. It should be noted that at 430 nm, there is no distinct shoulder characteristic of the azo form. We can note a shoulder at 520 nm which is absent in the spectrum in solution. This shoulder at 520 nm can be attributed to a donor–acceptor charge transfer band.

We have used transmission FT-IR spectroscopy to probe the surface chemical reactions on illuminated TiO₂ surface. The temporal evolution of FT-IR spectra of AO7–TiO₂ complex during irradiation with visible light is presented in Fig. 3. After 40 min of exposure, the FT-IR spectrum is largely modified with respect to the initial spectrum of AO7. The bands at 1508 and 1257 cm⁻¹ which are linked to δ (N–H) and ν (C–N), respectively [8] disappear completely in the spectrum $t = 40$ min and new bands appear

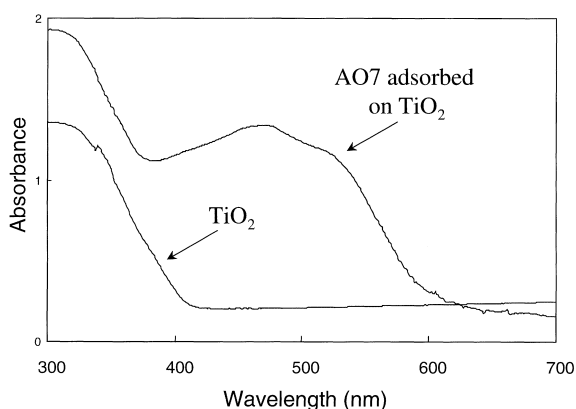


Fig. 2. Diffuse reflectance electronic absorption spectra of bare TiO₂ and AO7 adsorbed onto TiO₂.

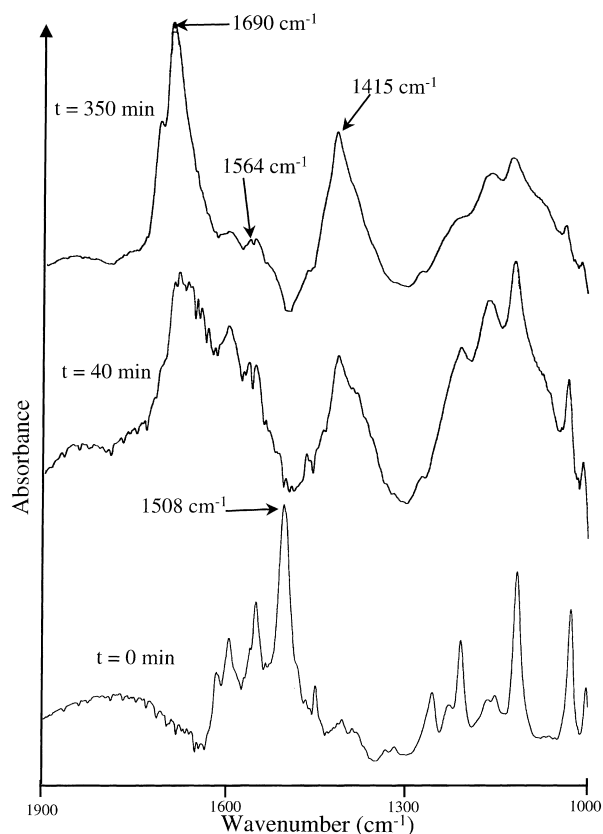


Fig. 3. Temporal evolution of FT-IR spectra during irradiation with visible light ($\lambda = 442$ nm).

in the 1600–1700 cm⁻¹ range and near 1400 cm⁻¹. At 1415 cm⁻¹, we observe a band that increases with irradiation time. Between 1600 and 1700 cm⁻¹, the intensity of the broad band with many shoulders increases with irradiation time too. In this region, the resolution of the spectrum at $t = 350$ min is better than in the spectrum at $t = 40$ min. This can be attributed to the variations of the surface concentrations in degradation products. In the final spectrum at $t = 350$ min, we also note a band at 1690 cm⁻¹ with a shoulder at 1715 cm⁻¹ and a band at 1415 cm⁻¹.

From FT-IR spectroscopic data, we can deduce the following points: (i) concentrations in N–H and C–N groups revealed by the bands at 1508 and 1257 cm⁻¹, respectively, decrease rapidly with irradiation time; (ii) the oxidative attack results first in the cleavage of chromophoric part of the AO7 molecule; (iii) several carboxylic and carbonyl groups are formed during the process revealed by the appearance of bands in the 1650–1750 cm⁻¹ area.

4. Discussion

In order to identify the degradation products present on the TiO₂ surface we compared FT-IR spectra available in the literature and standard prepared samples of species that are possibly formed during the photooxidation of AO7. In

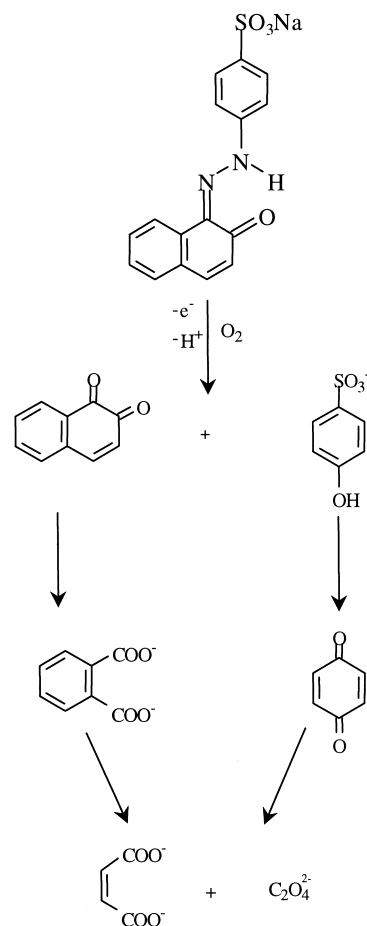
the final spectrum, two main bands are situated at 1690 and 1415 cm^{-1} . Other bands appear at 1600, 1564, 1553, 1164 and 1124 cm^{-1} . The band at 1690 cm^{-1} can be linked to species containing a carbonyl group.

It is known that oxidative attack of an azo dye from the phenylazonaphthol family leads to benzene sulfonate and naphthoquinone as primary degradation products. We could expect to form this species, but the probability to observe naphthoquinone on an illuminated TiO_2 surface is poor since the surface is very reactive and this compound is known to be unstable. It is more likely that phthalic acid is formed from the naphthalenic ring of AO7 molecule. The stretching vibration mode of the carbonyl in isolated phthalic acid is located at 1682 cm^{-1} , but when it interacts with a surface Lewis acidic Ti^{IV} center, the frequency of the band is shifted toward lower frequencies. FT-IR spectrum of phthalic acid adsorbed on TiO_2 obtained from aqueous suspension shows a broad band at 1550 cm^{-1} , but no band at 1690 cm^{-1} . Our spectrum is in good agreement with the one reported by Tunesi and Anderson [10] in a deuterated aqueous TiO_2 suspension. Therefore, we can exclude that the band at 1690 cm^{-1} (with its shoulder at 1715 cm^{-1}) in the final spectrum at $t = 350$ min is linked to phthalic acid adsorbed on TiO_2 . Thus, phthalic acid is perhaps an intermediate product, but not a final degradation product.

Destruction of the aromatic ring should lead to several aliphatic carboxylic acids. The ultimate C_2 compound is oxalate. The spectrum of oxalic acid adsorbed on TiO_2 exhibits bands at 1720, 1690, 1400 and 1250 cm^{-1} is close to those reported by Hug and Sulzberger [11].

In the literature, a few spectroscopic data of aliphatic carboxylic acids adsorbed on TiO_2 are available. Formate adsorbed on TiO_2 shows bands at 1560 and 1360 cm^{-1} due to ν_{as} (COO^-) and ν_{s} (COO^-), respectively [12]. The FT-IR spectrum of acetate [13] adsorbed on TiO_2 exhibits bands at 1555 and 1420 cm^{-1} . We attribute the bands in the range 1100–1170 cm^{-1} to oxygenated sulfur derivatives [14]. The shoulders at 1420, 1365, 1385 can be linked to CO_x surface species (for example, CO_2^- , CO_3^{2-} , HCO_3^-) [15–17]. The fact that no reaction occurs for the complex AO7– TiO_2 in the dark or in the absence of TiO_2 shows that the degradation process implies TiO_2 and the excited state $^1\text{AO7}^*$. It is known from studies of the photosensitization of wide band gap semiconductors that after absorption of a photon, an anchored dye can inject an electron into the conduction band of the semiconductor from its excited state if the energetic of the system allows it.

Diffuse reflectance electronic absorption spectrum in Fig. 2, suggests that adsorbed AO7 exists under its hydrazone tautomer. No shoulder at 430 nm characteristic of the azo tautomer is present; instead, the absorption maximum is located at 480 nm near the one of the hydrazone form. But, the strongest evidence for the presence of the hydrazone form on TiO_2 comes from FT-IR spectroscopic data. In the FT-IR spectrum of AO7 adsorbed on TiO_2 only the bands of the hydrazone form are present [8].



Scheme 1.

After photoinjection of an electron in the conduction band of TiO_2 , the cation radical formed from the hydrazone form can undergo rapid deprotonation to create the radical form which can interact with molecular oxygen. A proposed degradation mechanism is illustrated in Scheme 1. Other active oxygen species can be involved in the process of photooxidation of AO7. It has been suggested that phenylazonaphthol dyes can photosensitize their own degradation through the generation of singlet molecular oxygen. But, we believe that singlet molecular oxygen plays no role in the photodegradation of AO7 and this for two reasons: (i) during the direct photolysis of AO7 in the absence of TiO_2 we observe no degradation; (ii) we expect that the creation of AO7 triplet state is extremely improbable since the AO7 singlet state has an ultrashort lifetime, because of the ultrafast relaxation by electron injection in the conduction band of TiO_2 .

Fig. 4 shows the temporal evolution of the absorbance of the bands at 1508 (AO7), 1690, 1415 and 1564 cm^{-1} (degradation products). The complete decrease of the absorbance of the band at 1508 cm^{-1} reflects the total elimination of AO7 from the TiO_2 surface. No bands due to degradation products appear in this area. We can also note the growth of the bands at 1690 and 1415 cm^{-1} that follows a first order kinetic. The temporal evolution of the intensity of the band

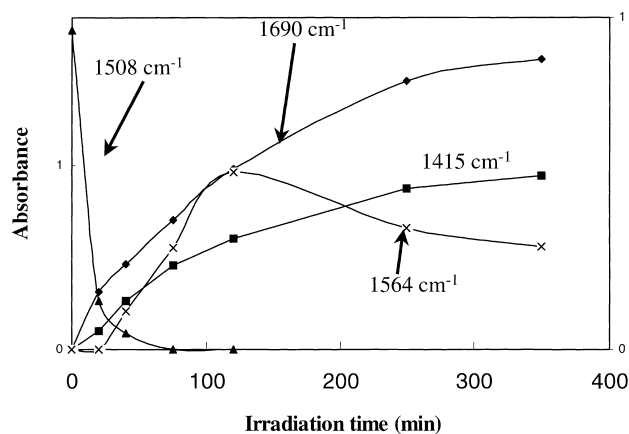
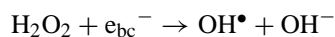
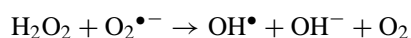
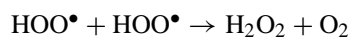
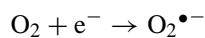


Fig. 4. Temporal evolution of the absorbance of the main FT-IR bands during photooxidation of AO7: AO7 (1508 cm^{-1}); acetate (1415 cm^{-1}); formate (1564 cm^{-1}); oxalate (1690 cm^{-1}).

at 1564 cm^{-1} differs from those of the bands at 1690 and 1415 cm^{-1} . After the total disappearance of the dye, the intensity of the band at 1564 cm^{-1} stops to increase. At the opposite, the formation of degradation products still continues even if the system can not absorb photonic energy anymore since no colored compounds are present onto TiO_2 surface. Between $t = 20$ and $t = 120$ min, the formation of formate follows a zero order kinetics; this phenomenon reflects that the process is step limited by the supply of molecular oxygen to the TiO_2 surface. Experimentally, this leads to a zero order kinetic for the growth of the absorbance at 1564 cm^{-1} . We have noted the similar kinetic behavior for the para isomer of AO7 dye (Acid Orange 20). It is still unclear if the slower step is the rate of adsorption/desorption process or the rate of electron transfer from the conduction band to molecular oxygen. Thus, an important role of molecular oxygen is to scavenge the electron of the conduction band to avoid the recombination with the cation radical. The temporal evolution of the FT-IR band suggests at least two mechanisms, one linked to the light (electron photoinjection process) and another one that occurs in the dark (surface chain radical mechanism). In this process, molecular oxygen has also a chemical role. The superoxide anion radical formed by the trap of an electron from the conduction band of TiO_2 can lead to several active oxygen species through the following reactions.



Thus, hydrogen peroxide, perhydroxyle and hydroxyl radicals can be formed. The generation of hydroxyl radicals requires the reduction of O_2 by the electron of the conduction band. The contribution of these oxygen species to

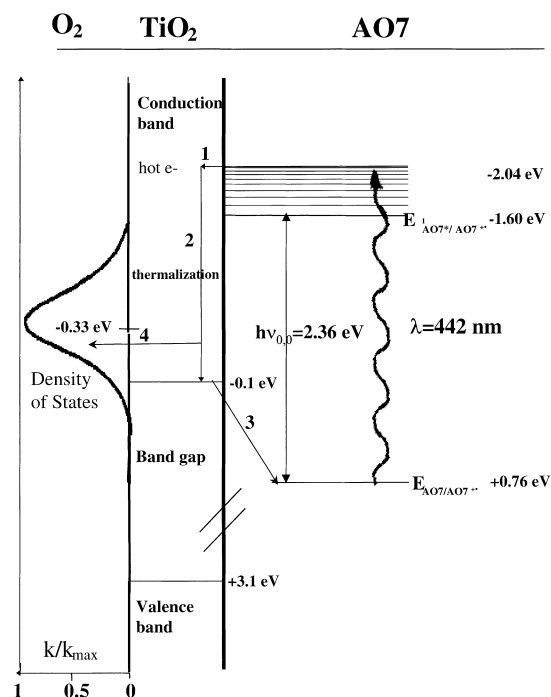


Fig. 5. Energetic level diagram AO7– TiO_2 – O_2 interface. 1: electron injection; 2: thermalization; 3: back electron transfer; 4: scavenging of conduction band electron by molecular oxygen.

the photooxidation process is far to be elucidated. Several steps are necessary for the formation of these species and it is likely that neutral molecular oxygen or superoxide are sufficient for the degradation of AO7 dye.

It is not easy to predict the energy level of a donor adsorbed on a semiconductor surface. Even, if it is not rigorous to take redox potential from homogeneous solutions it seems to be the best approximation for phenomena occurring on semiconductor surfaces. The energy of the excited state $^1\text{AO7}^*$ can be obtained by intercrossing the absorption and emission spectra of AO7; Kamat et al. [18] have measured the value of $h\nu_{0,0}$ to be 2.36 eV; the redox potential of the couple $\text{AO7}/\text{AO7}^{+\bullet}$ is 0.76 V NHE $^{-1}$ [19]. Therefore, the energetic level of the singlet excited state of $\text{AO7}/\text{AO7}^{+\bullet}$ lies more than 1 eV over the fundamental band edge of the TiO_2 conduction band. Fig. 5 shows an energetic diagram of the photophysical events. The efficiency of the process of AO7 photooxidation is determined by the competition between forward electron transfer and back electron transfer. A key step in the photooxidation process of AO7 is the creation of the cation radical $\text{AO7}^{+\bullet}$ which triggers degradation. The photoinjection process for the formation of the cation radical $\text{AO7}^{+\bullet}$ is in competition with other relaxation channels of $^1\text{AO7}^*$ as radiative and nonradiative decay or recombination of injected electrons with $\text{AO7}^{+\bullet}$ for the recovery of the fundamental electronic state. We have recently measured using two-color femtosecond pump probe spectroscopy the rate of forward and back electron transfer by monitoring the appearance of electrons in the conduction band of TiO_2 .

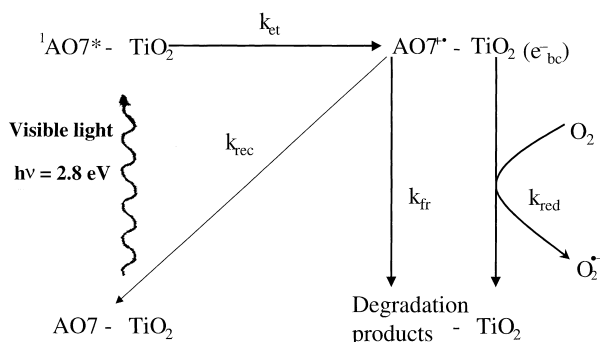


Fig. 6. Different kinetics pathways during the early events of the photo-degradation process.

The electron injection process occurs within the duration of the laser pulse (<150 fs). At the opposite the back electron transfer time is much slower and occurs in the nanosecond regime [20]. We have also noticed by following the recovery of the ground state and the decay of the excited state that the lifetime of $^1\text{AO7}^*$ in aqueous solution is very short (10 ps). This short time scale is attributed to the excited state relaxation via a proton transfer between the two tautomer forms. From Fig. 6, the efficiency or the quantum yield for the formation of the cation radical $\text{AO7}^{\bullet+}$ is given by the simple relationship $\phi = k_{\text{inj}} / (k_{\text{inj}} + k_{\text{rec}})$, where k_{inj} is the rate of electron injection and k_{rec} is the rate of recombination. A strategy to increase the efficiency of the $\text{AO7}^{\bullet+}$ formation is to accelerate the electron transfer rate to molecular oxygen and, thus, minimizing back electron transfer rate. Recently, a dramatic increase of the electron transfer rate for the electron conduction band of TiO_2 to an acceptor as molecular oxygen was observed, when bidentate surface complexes are present on TiO_2 [21,22]. It was shown that AO7 adsorption on TiO_2 leads to an inner-sphere surface complex. There is a strong electronic interaction between the molecular state and the TiO_2 solid state via the carbonyl group and the bidentate binuclear coordination type with the sulfonate group of AO7 [8]. A cardinal factor for the process yield is the electron transfer step to O_2 . This molecular species can strongly avoid the recombination between the electron conduction band and the cation radical $\text{AO7}^{\bullet+}$. The chemisorption of AO7 on TiO_2 has a favorable effect on the yield of the photooxidation process by eliminating the surface states within the band gap and, thus, enhancing electron transfer rate to O_2 .

5. Conclusion

AO7 is photooxidized on TiO_2 surfaces by an electron injection process in the conduction band of TiO_2 induced by visible light. Kinetics of disappearance of AO7 dye has been followed by the decrease of the most intense FT-IR

band at 1508 cm^{-1} linked to the N–H bending vibration mode of the chromophore part of the hydrazone form. This tautomer form triggers the photooxidation process via a deprotonation of the labile hydrogen borne by the C=N–N–H moiety. Oxalate, acetate, carbonates and oxygenated sulfur compounds were identified as the final degradation products. The results suggest that there are at least two mechanisms for photooxidation of AO7, one linked to light (electron photoinjection process) another one which can occur in the dark (surface chain radical mechanism) and that the molecular oxygen supply onto TiO_2 surface is the rate limiting step of the overall photooxidation process. For a better understanding of the electron transfer reactions for the removal of dyes by the photosensitization pathway, information should be taken from the active research area concerning dye-sensitized semiconductors for solar energy conversion.

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