Journal of Catalysis 269 (2010) 404–410

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Influence of hydrogen bonding upon the TiO_2 photooxidation of isopropanol and acetone in aqueous solution

Carolina Salazar [a], Mark A. Nanny [a,b,*]

[a] School of Civil Engineering and Environmental Science, College of Engineering, University of Oklahoma, Norman, OK 73019, USA
[b] Institute for Energy and the Environment, College of Earth and Energy, University of Oklahoma, Norman, OK 73019, USA

ARTICLE INFO

Article history:
Received 16 October 2009
Revised 23 November 2009
Accepted 25 November 2009
Available online 4 January 2010

Keywords:
Acetone
Isopropanol
pH
TiO_2 photocatalysis
TiO_2 surface hydroxyl groups
Hydrogen bonding

ABSTRACT

This study investigates the aqueous photocatalytic degradation of small polar organic compounds (SPOCs) that bear hydrogen-bonding capabilities but do not readily adsorb to the TiO_2 catalyst. The effect of pH on the TiO_2 surface hydroxyl speciation and surface acid/base equilibria was used to elucidate the possible role of hydrogen-bonding interactions in the degradation of acetone and isopropanol in aqueous TiO_2 photocatalytic systems. The kinetic parameters describing the decomposition of these two model compounds were obtained by gas chromatographic analysis of their photoreaction systems and interpreted on the grounds of the Brönsted acid/base properties of the TiO_2 surface speciation and solute hydrogen-bonding numerical scales. The results showed that the fastest initial degradation rates of acetone and isopropanol occurred in a pH range where the optimal conditions for adsorption through hydrogen bonding to the TiO_2 surface and optimum concentration of hydroxyl radicals ($OH^{\cdot}$) coincide. The fastest degradation constants were observed at pH 6.04 and 8.61 for acetone and isopropanol, respectively. The hypothesis of hydrogen bonding to surface hydroxyl groups presented in this study challenges the common assumption that these model compounds do not adsorb to surface sites, and that their oxidative pathways of degradation only occur via homogeneous-phase reaction with free $OH^{\cdot}$ radicals.

1. Introduction

Drinking and hygiene water sustainability is a current concern due to the rapid pace of global urbanization and the vast coverage gap between urban and rural areas worldwide. Therefore, water recycling has become a necessity to alleviate the fragile state of most of the planet's water resources and has prompted the search for viable and efficient alternatives for wastewater treatment. In response to this search, advanced oxidation processes (AOPs), such as UV/TiO_2 heterogeneous photocatalysis, have arisen and are being extensively investigated.

The photocatalytic oxidation of small polar organic compounds (SPOCs) such as isopropanol and acetone by UV-illuminated TiO_2 has been more widely studied in the gas/solid interfaces [1–17] than in the liquid/solid interfaces [18–25]. This is probably due to the fact that they are the major contaminants in indoor air and air streams. However, their presence in water, even at low concentrations, is also a concern when hygiene and drinking water standards are desirable. The removal of isopropanol and acetone to acceptable levels has already been reported as a challenge in an advanced water recovery system developed by the National Aeronautics and Space Administration (NASA) [26]. These compounds remain in treated effluents after physical, biological, and chemical processes involved in wastewater treatment plants or water recovery systems [26,27]. Therefore, a better understanding on the TiO_2-mediated photocatalytic oxidation of SPOCs (e.g., isopropanol and acetone) is necessary if the ultimate goal is to apply this promising technique for the final polishing of waste- and graywater in order to attain hygiene and drinking water standards.

A combination of adsorption isotherms, infrared spectroscopy, temperature programed desorption, and gas chromatographic methods have studied the adsorption of acetone and isopropanol in solid/gas systems employing both dehydroxylated and hydroxylated TiO_2 surfaces [1,5,6,8,10,28,29,17]. These studies demonstrated that acetone and isopropanol are molecularly adsorbed in fully dehydroxylated TiO_2 surfaces through the formation of coordinate bonds with Ti^{4+} ions by utilizing their free electron pairs of the oxygen atoms in their respective functional groups.

On the other hand, on partially hydroxylated TiO_2 surfaces, reversible physisorption of these two substrates also takes place and occurs by hydrogen bonding with surface hydroxyl groups [1,29]. This mode of adsorption was reported in TiO_2/gas systems for other aliphatic alcohols such as methanol, ethanol, and 1-propanol [30,31].

---

* Corresponding author. Address: School of Civil Engineering and Environmental Science, College of Engineering, University of Oklahoma, Norman, OK 73019, USA. Fax: +1 405 325 4217.
E-mail address: nanny@ou.edu (M.A. Nanny).

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.11.025

Contrary to solid/gas studies, the chemisorption of isopropanol and acetone in aqueous media should be negligible. In TiO_2/aqueous systems, isopropanol and acetone do not favorably compete with water for chemisorption to the TiO_2 surface. Therefore, alkoxide complexes ($\equiv$Ti–OR) or molecularly adsorbed species coordinated to the Ti^{4+} ions observed at the TiO_2/gaseous interface are completely absent in TiO_2/aqueous systems. It is known from relative adsorption strength studies in TiO_2/gas systems that isopropanol does not displace the coordinatively adsorbed water and that water has the ability to dislodge acetone from its Ti^{4+} adsorption center [1,29]. In addition, Mandelbaum et al. [22] did not observe any feature as detected by ATR-FTIR demonstrating alcohol chemisorption on TiO_2 in aqueous media.

It was suggested that since in aqueous media alcohols do not chemisorb to the catalyst surface the reaction between alcohols and hydroxyl radicals ($OH^{\cdot}$) occurs within the thin interfacial layer vicinal to the surface [19,22]. We believe that this lack of coordination to the Ti^{4+} ions does not preclude that their adsorption in solid/aqueous systems may take place on the layer of surface hydroxyl groups formed after water dissociative chemisorption. Therefore, we suggest that in the case of TiO_2 in contact with an aqueous solution of acetone or isopropanol (and in the absence of any strongly bound species) hydrogen bonding between either of both substrates and the surface hydroxyl groups may be regarded as a prominent adsorption mechanism.

This suggestion is reasonable considering that this outer sphere interaction has been already observed for aliphatic alcohols in TiO_2/gas-phase studies using pre-hydroxylated oxide samples [29–31]. Nevertheless, to the best of our knowledge, no study has been conducted to determine the possible key role that hydrogen-bonding capacities of these two compounds could play on their adsorption and subsequent degradation in TiO_2/aqueous systems. Therefore, the investigation of this hydrogen-bonding hypothesis was undertaken in this study. It would be interesting to obtain insight on any possible role that surface phenomena may play on their TiO_2/aqueous photocatalytic degradation which would challenge the widespread conception that they do not adsorb to surface sites and merely degrade via free $OH^{\cdot}$ radicals in the bulk solution [32–34].

In this study, the role played by pH in determining the photodegradation kinetics for two SPOCs, acetone and isopropanol, was investigated. We hypothesized that the maximum in the rate of degradation for each of these compounds would occur at conditions where the surface speciation present at a given pH is optimal for both the hydrogen bonding of the model substrate and the production of hydroxyl radicals. Since $OH^{\cdot}$ radical production is higher in neutral and, especially, at alkaline media [35] the fastest degradation rates of our model compounds would occur within a neutral to alkaline pH range.

In order to evaluate our hypothesis, the analysis of the kinetic data was done on the basis of numerical scales of hydrogen-bonding capacities of our substrates [36] and the effect of pH on the surface hydroxyl group speciation according to a multisite proton adsorption modeling of the TiO_2/solution interface [37–40]. This type of analysis is lacking in the interpretation of photocatalytic results obtained for organic compounds that may adsorb to the TiO_2 surface through outer sphere interactions.

2. Experimental section

2.1. Materials

In all experiments, titanium dioxide (TiO_2) Degussa P25 was used as the photocatalyst without modification (Lot No. 2047, BET surface area = 50 ± 15 m^2/g, average particle size = 21 nm, Degussa Corporation). Isopropanol (ISP), ($(CH_3)_2CHOH$), and acetone (ACE), ($(CH_3)_2CO$) were purchased from Aldrich. These commercial materials were of 98% purity or higher, and used as received. NaOH (97% purity) and HNO_3 (90% purity) were obtained from Fisher Scientific and used for pH adjustment of the reaction suspensions. Nanopure water (18.1 MΩ cm) from an Infinity™ ultrapure purification system (model D8961, Barnstead) was used for the preparation of all solutions.

2.2. Photooxidation apparatus

The photooxidation apparatus consisted of a 450 W medium pressure mercury-vapor lamp (Ace Glass, Cat. 7825-34) positioned within a double-walled quartz immersion well (Ace Glass, Cat. 7874-35) with inlet and outlet water lines. The photochemical lamp was plugged to a 450 W power supply (Ace Glass, Cat. 7830-60). A water-flow power cut-off (Ace Glass, Cat. 2162-14) was used for safety in the event of a water or main power failure. The cooling water jacket was used to remove some of the lamp heat and maintained a temperature between 25 and 27 °C inside the steel bench cabinet (dimensions: 89 cm high × 92 cm wide × 61.5 cm deep) where the photochemical reaction equipment was operated. A cooling fan was located on top of the lamp housing for air movement.

The reaction solution (20 mL) was contained in a cylindrical cap-sealed quartz reaction vessel (Ace Glass, Cat. D116912, 25 mL capacity, 10 cm long × 22 mm O.D.; screw cap with ¼″ hole, thread GL25). The screw cap was fitted with a PTFE/silicone rubber septum (VWR, Cat. 66010-751). During the photocatalytic reaction the quartz reaction vessel was placed in a motor-driven rotating stirrer (Scientific Industries, Inc., Cat. 3-163-404) to ensure a complete and continuous mixing while it was directly exposed to the lamp. This experimental setup permitted simultaneous irradiation of several reaction vessels.

2.3. Sample preparation and photocatalytic experiment

The reaction samples were prepared by suspending 2 g/L of TiO_2 powder in 20 mL of freshly prepared aqueous solution of isopropanol or acetone. Preliminary experiments where different quantities of TiO_2 (0.3–3.0 g/L) were used to degrade isopropanol and acetone (100 ppm) showed that the optimum catalyst concentration to be used is 2 g/L based on the rate constant calculations. All solutions were prepared in duplicate. Control solutions (where no catalyst was added) were prepared under the same conditions and underwent the same treatment as the reaction samples to determine the contribution of a possible competing degradation pathway (direct photolysis) to the degradation of acetone and isopropanol.

Initial concentrations of our model compounds in the aqueous TiO_2 suspensions ranged between 1.56×10^{-3} and 1.64×10^{-3} M. These values were selected in order to simulate typical concentrations of both compounds in wastewater [26,27], yet high enough to give a good signal to noise ratio in the gas chromatograph experiments during the irradiation times used in our studies.

The pH values of the suspensions were measured with a digital pH meter (Orion PerpHect, model 350, Fisher Scientific, Cat. 13-642-629) and a needle combination pH microelectrode (Microelectrodes, Inc., Cat. MI-414B). The pH was adjusted to the desired value by the addition of NaOH or HNO_3 using a 10 μL microsyringe (Shimadzu, Cat. 221-34618-00). The suspensions were placed in the dark, shielded with aluminum foil, and allowed to equilibrate overnight at 10 °C.

After irradiation at regular time intervals, the samples for analysis were withdrawn with a syringe (Perfektum Micro-mate interchangeable syringe, luer-lock tip, 2 mL, Fisher Scientific, Cat. 14-825-1A) and filtered through a 0.1 μm nylon membrane (Osmonics

Inc., Fisher Scientific, Cat. R01SP01300) fitted in a 13 mm-filter holder (Millipore, Fisher Scientific, Cat. XX3001200). The filtrate was transferred to two autosampler vials containing fixed 100 μL glass inserts (VWR, Cat. 66065-262) which were capped (open-top cap, 8-425 screw thread, with 8 mm PTFE/silicone septa, VWR, Cat. 66030-420) and stored in the dark at 10 °C until gas chromatographic analysis (each vial was injected once).

Dissolved oxygen (DO) in the suspensions was not controlled, but monitoring of its concentration showed that it was still present at the maximum irradiation time selected to sustain the photocatalysis reaction (3.1 ± 0.5 ppm DO at 25.3 ± 0.5 °C and $t = 15$ min). DO was measured using a fiber optic oxygen sensor system equipped with a spectrofluorometer (Ocean Optics, Cat. USB4000-FL-450), a pulsed blue LED light source (Ocean Optics, Cat. USB-LS-450), and the OOISensors software (Ocean Optics). A 18-gauge needle probe containing the 300-μm fiber oxygen sensor (Ocean Optics, Cat. FOXY-18G-AF) and a RTD hypodermic temperature probe (Ocean Optics, Cat. USB-LS-450-TP16) were used for DO and temperature readings, respectively.

2.4. Gas chromatographic analysis

The degradation of isopropanol and acetone was followed by gas chromatography using a Shimadzu GC-17A equipped with a fused silica capillary column (Supelcowax™-10, polyethylene glycol stationary phase, 30 m length × 0.32 mm i.d. × 1.0 μm film thickness, Aldrich) and a FID detector (ultrahigh purity helium used as carrier gas). An oven temperature program of 60 °C (2.0 min) to 80 °C @ 5 °C/min, injector and detector temperatures of 200 °C, and 1 μL injection volume (split 15:1) were selected for the chromatographic analysis.

The concentration of isopropanol and acetone in the filtrates was calculated by seven-point external standard calibration curves using freshly prepared standard solutions.

Acetone was the only reaction product of isopropanol photodegradation detected in the liquid phase by gas chromatography. A peak eluting at $R_t = 0.8$ minutes, probably corresponding to a product of acetone photodecomposition, was also observed in the chromatograms but it was not identified. This peak only accounts for 0.12–0.32% of the total percent area in the chromatograms obtained under our instrumental conditions.

2.5. Determination of kinetic parameters

The photodegradation modeling of acetone and isopropanol was performed using a program written in Mathematica 5.2 where the experimental data (molar concentration versus time) was related to mechanistic models expressed as the integrated rate equations for zero- and first-order reactions. A least-square analysis was used to determine the best fit and the model kinetic parameter (i.e., the rate constant). Photooxidation initial rates were measured within the first two half-life periods.

3. Results and discussion

3.1. Effect of pH upon the photocatalytic degradation of acetone and isopropanol

The influence of the solution pH on the photocatalytic degradation of isopropanol and acetone was examined separately for both compounds at three different pH values (4.10, 6.04, and 8.61). This experimental pH range was selected to bracket between the pK_a values of the surface hydroxyl groups on TiO_2 (see Eqs. (1) and (2)). Fig. 1 illustrates the results obtained in these experiments. Initial rates calculated by fitting the experimental data are given in Table 1. The analysis of the data indicates that acetone and isopropanol decompositions occur through mechanisms of first- and zero-order, respectively. Acetone exhibited the fastest degradation rate at pH 6.04 while for isopropanol it was observed at 8.61.

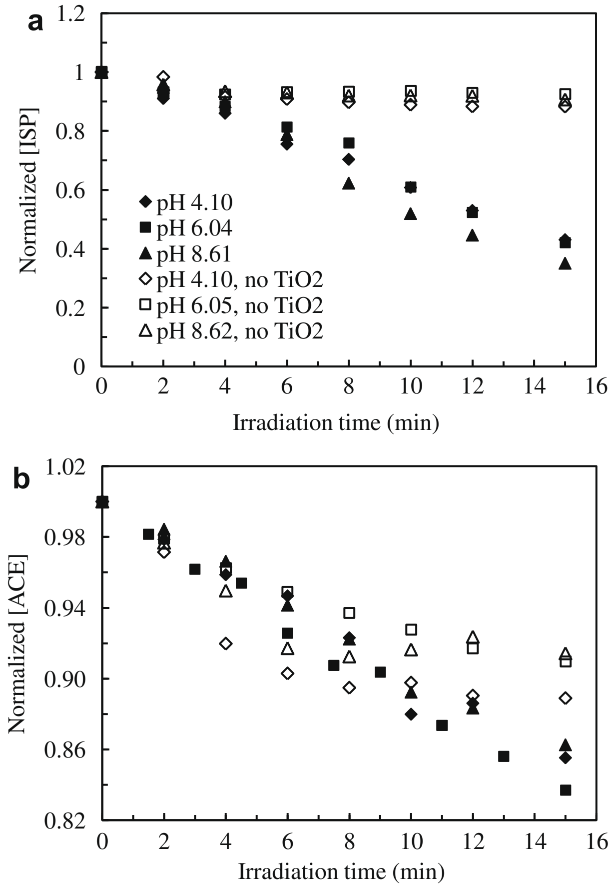

Fig. 1. Effect of pH upon the UV/TiO_2 heterogeneous photodegradation (filled symbols) and the direct photolysis (open symbols) of (a) isopropanol and (b) acetone in aqueous solution. pH conditions: (◆◇) pH 4.1, (■□) pH 6.0, (▲△) pH 8.6 (TiO_2, 2 g/L; initial concentrations, $[ISP]_o = (1.61–1.64) \times 10^{-3}$ M, $[ACE]_o = (1.56–1.57) \times 10^{-3}$ M).

The current thinking on the photodegradation of SPOCs [32–34] (i.e., aliphatic alcohols) cannot explain the results outlined above. If the photodegradation of substrates that do not strongly adsorb to the surface merely occurs through the reaction with hydroxyl radicals in the solution bulk then the maximum in the degradation rates of both isopropanol and acetone would be observed at the most alkaline pH used in our studies.

We agree that the hydroxyl radicals are probably the species responsible for the initial photodecomposition steps of substrates that do not strongly adsorb to the surface of TiO_2. However, we speculate, based on our findings for acetone and isopropanol, that other factors also determine their photooxidation which is operative on the catalyst surface. The trend observed in this study for the dependence of degradation rates of isopropanol and acetone with solution pH can indicate the possible role of TiO_2 surface phenomena on the adsorption and degradation of these model compounds.

In order to give a simple explanation for the observed results the multisite-protonated model proposed by Hiemstra et al. [37–39] was adopted. Therefore, it was assumed that the behavior of the TiO_2/solution interface for our particular system is dictated by the properties of the two distinctive surface hydroxyl groups formed upon dissociative water chemisorption: the singly coordi-

Table 1
Effect of pH on the initial rates of acetone (k_{ACE}) and isopropanol (k_{ISP}) degradation in UV-irradiated TiO_2 suspensions.[a]

	Initial solution pH		
	pH 4.10	pH 6.04	pH 8.61
k_{ACE} (min^{-1})	$(1.05 \pm 0.07) \times 10^{-2}$	$(1.21 \pm 0.05) \times 10^{-2}$	$(1.04 \pm 0.06) \times 10^{-2}$
k_{ISP} ($mol\ L^{-1}\ min^{-1}$)	$(6.22 \pm 0.09) \times 10^{-5}$	$(6.2 \pm 0.2) \times 10^{-5}$	$(7.5 \pm 0.3) \times 10^{-5}$

[a] Experimental conditions are given in Fig. 1.

nated or terminal OH group ($\equiv$Ti–OH$^{1/3-}$) and the doubly coordinated or bridging OH group ($\equiv$OH$^{1/3+}$) [37–41].

According to the multisite proton adsorption modeling of the TiO_2/solution interface each hydroxyl group has its corresponding intrinsic proton dissociation constant and, therefore, the pH of the aqueous medium has an effect on the surface speciation and the resulting charging behavior of the oxide surface. The surface equilibria of the $\equiv$Ti–OH$^{1/3-}$ and $\equiv$OH$^{1/3+}$ hydroxyl groups and their corresponding pK_a values (for Degussa P25 TiO_2) are given in Eqs. (1) and (2) as reported by Rodríguez et al. [40].

$$\equiv\text{Ti}{-}\text{OH}_2^{2/3+} \leftrightarrow \equiv\text{Ti}{-}\text{OH}^{1/3-} + \text{H}^+ \quad \text{p}K_{a1} = 5.38 \tag{1}$$

$$\equiv\text{OH}^{1/3+} \leftrightarrow \equiv\text{O}^{2/3-} + \text{H}^+ \quad \text{p}K_{a2} = 7.60 \tag{2}$$

Based on the surface site distribution calculations as a function of solution pH, Rodríguez et al. [40] suggested that the surface groups with the smallest residual charge numbers (that is, the $\equiv$Ti–OH$^{1/3-}$ and $\equiv$OH$^{1/3+}$ surface groups) prevail at pH values above and below the pH of zero point charge (pH$_{zpc}$) of TiO_2 (pH$_{zpc}$ = 6.50, [40]), respectively. Since the calculations of these authors also show that the fractions of $\equiv$Ti–OH$_2^{2/3+}$ and $\equiv$O$^{2/3-}$ contributing to the net surface charge only became important under the effect of ionic strength, in this analysis we will assume that the concentrations of these surface groups are minute in our photocatalytic systems (that is, zero ionic strength is assumed). The effect of ionic strength on the photocatalytic degradation of isopropanol and acetone will be the subject of a future publication.

A simple interpretation of our experimental results on the basis of this current model of the surface behavior can serve as an evidence that adsorption of our model compounds to the TiO_2 surface sites may occur through hydrogen bonding to the surface hydroxyl groups.

If our hypothesis of hydrogen bonding to the surface hydroxyl groups is correct, a substrate such as isopropanol would have the capability to adsorb on TiO_2 in all the ranges of pHs. By orienting the oxygen or hydrogen atom of its polarized hydroxyl group, isopropanol can approach the surface sites with residual positive or negative charge. In addition, considering that the model alcohol has hydrogen donor ($\alpha^H = 0.33$, [36]) and acceptor ($\beta^H = 0.56$, [36]) capabilities several modes of adsorption can be envisioned with the surface species bearing Brönsted acid/base properties. Two possible modes of isopropanol adsorption are represented in Fig. 2a and b. On the other hand, acetone, which only possesses the ability to accept a proton through its carbonyl group ($\alpha^H = 0.04$, $\beta^H = 0.49$; [36]), would be able to approach positively charged surface sites with acidic character because only the negative end of its dipole can be exposed to the charged surface (Fig. 2c and d). Hence, acetone adsorption to the TiO_2 surface is more limited compared to isopropanol since it will mostly occur at pH $\leqslant$ pH$_{zpc}$ where the surface groups with acidic character are present.

The explanation of our data would not be complete without considering the pH dependence of the formation of the species responsible for the degradation of our model compounds. Since the production of OH$^{\cdot}$ radicals occurs by trapping of photogenerated free holes (h_f^+) in surface hydroxyl groups [42], it is reasonable to suggest that h_f^+ react faster with negatively charged surface hydroxyl groups present at neutral and alkaline pHs [33]. Therefore, surface hydroxyl radicals which can initiate the oxidation reactions in both acetone and isopropanol [18–20,22,24,25,43], would be formed at a higher rate in neutral and, especially, at alkaline media [35].

On the basis of the two aspects of our rationale, the faster reaction rates of isopropanol and acetone decomposition would be expected to occur in a pH range where optimum conditions for adsorption to the TiO_2 surface and optimum concentration of surface OH$^{\cdot}$ radicals coincide. This prediction is consistent with the results obtained.

In the case of isopropanol, adsorption modes through hydrogen bonding with surface sites may involve $\equiv$Ti–OH$^{1/3-}$ and $\equiv$OH$^{1/3+}$ groups. Since these surface sites are the most abundant sites at pH above and below the pH$_{zpc}$ [40], respectively, this substrate possesses fewer restrictions to adsorb to the surface at any of the pH values used in this study.

The above would also explain why zero-order kinetics is observed for the decomposition of isopropanol. The fact that the rate of degradation does not depend on isopropanol concentration (which ranges between 1.61 and 1.64×10^{-3} M) may be an indication that saturation coverage of the hydrogen-bonding active sites is attained. This can be illustrated if the number of available acidic hydroxyl groups (2.97×10^{-6} mol m^{-2}) and the specific surface area (51.4 m^2 g^{-1}) reported by Rodríguez et al. [40] for Degussa P25 TiO_2 are used to obtain their total concentration in our photocatalytic reaction systems. From these values it can be calculated that under the conditions used in our studies there are 3.15×10^{-4} moles of acidic OH groups per liter of solution compared to $(1.61–1.64) \times 10^{-3}$ moles per liter of isopropanol. A similar concentration of basic OH groups can be assumed based on the determination of Van Veen et al. [44]. As a result of the above, the principal factor influencing isopropanol photooxidation could be the concentration of active species (i.e., OH$^{\cdot}$ radicals) that are formed under the given experimental conditions, as previously suggested by Cunningham and Srijaranai [19] from an isotope-effect study. Therefore, the fastest degradation of isopropanol in

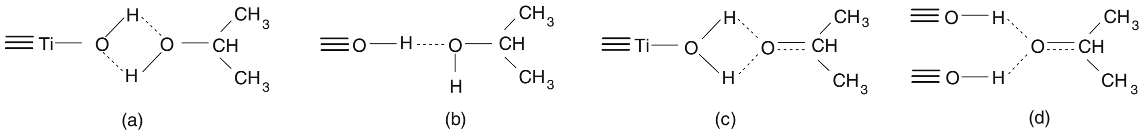

Fig. 2. Possible hydrogen-bonding structures of isopropanol and acetone on the TiO_2 surface in contact with their aqueous solution.

our photocatalytic system occurred at the most alkaline media (pH 8.61) where a higher concentration of surface hydroxyl radicals is expected.

On the other hand, adsorption of acetone is more restricted because it can only act as a hydrogen acceptor. Therefore, its mode(s) of adsorption onto the surface may only involve the acidic and positively charged $\equiv OH^{1/3+}$ and $\equiv Ti{-}OH_2^{2/3+}$ groups occurring at pH 4.10 and 6.04. However, the rate of degradation of acetone was found to be higher at pH 6.04 where the best compromise between suitable surface site for adsorption and abundance of hydroxyl radicals is attained.

A first-order reaction for the photocatalytic conversion of acetone may be an indication that its adsorption to the surface is the most determining factor for its optimal degradation. A possible justification is that the nature of the degradation products resulting from $OH^{\cdot}$ radical attack might prevent the saturation coverage of the TiO_2 surface with our model compound. Formic acid and acetic acid are possible oxidation products of acetone [43] that can form inner sphere complexes with Ti^{4+} ions which affects the surface density of hydrogen-bonding sites and the surface hydroxyl radical production. Formaldehyde, another plausible product [43], would have a lesser effect as a surface site competitor since it is a weaker hydrogen acceptor ($\beta^H = 0.33$, [36]) than the parent compound.

3.2. Direct photolysis studies

At this point it is necessary to evaluate the possibility of any contribution from direct photolysis in the decomposition of acetone and isopropanol in the suspensions before the validity of our hydrogen-bonding hypothesis can be ascertained.

Acetone and isopropanol are weakly absorbing compounds in the UV range at wavelengths below 350 and 250 nm, respectively [17] (molar absorption coefficient for acetone is $\varepsilon_{260nm} = 15.4$ $M^{-1}\,cm^{-1}$ [45] while for isopropanol it is $\varepsilon_{185nm} = 32$ $M^{-1}\,cm^{-1}$ [46]). Therefore, they may undergo decomposition through direct photolysis in their UV-irradiated aqueous solutions. Since these wavelengths are emitted by the medium pressure mercury lamp used in our studies, direct photolysis may be an alternative route for the decomposition of our compounds besides the TiO_2-mediated photooxidation in our heterogeneous photocatalytic systems. In order to determine the efficacy of this direct route compared to UV/TiO_2 photocatalysis, the occurrence of the former reaction (i.e., in the absence of TiO_2 catalyst) was investigated in solutions containing our model compounds at the same concentrations and initial pH conditions used in the heterogeneous photocatalytic experiments. Fig. 1 depicts a comparison of the efficacy of both methods for the treatment of our model compounds in water while Fig. 3 shows a comparison of the direct photolysis of acetone and isopropanol.

In Fig. 3 it can be observed that the conversion time profiles corresponding to the direct photolysis of both acetone and isopropanol do not conform to simple zero- or first-order kinetics. Therefore, the model parameters describing their direct degradation by UV light cannot be given.

The comparisons made in Fig. 1a show that under similar experimental conditions the photocatalytic reaction pathway is more effective than direct UV photolysis for the oxidation of isopropanol in aqueous solution at all the pH values tested in this study. Although acetone is the oxidation product of isopropanol under both treatment methods, its production is negligible through direct photolysis under the conditions used in our experiments. This is in agreement with the low yields of isopropanol UV photolysis reported in aqueous solution [46,47]. Therefore, we can assume that in the TiO_2-containing photocatalytic systems direct photolysis is not an important pathway of isopropanol degradation.

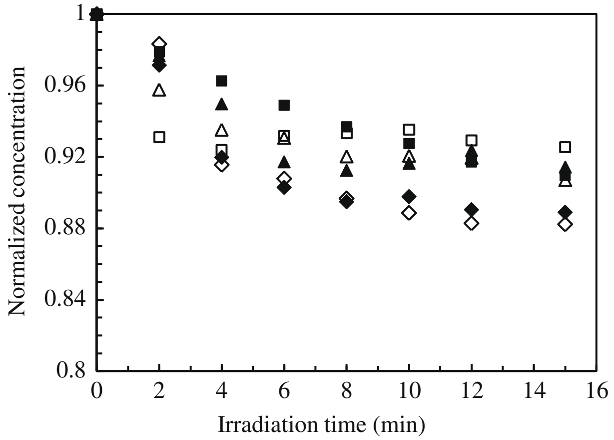

Fig. 3. Direct UV photolysis of acetone (filled symbols) and isopropanol (open symbols) in water under different pH conditions. (♦◇) pH 4.11, (■□) pH 6.05, (▲△) pH 8.62. Average initial concentrations: $[ACE]_o = (1.55 \pm 0.06) \times 10^{-3}$ M, $[ISP]_o = (1.64 \pm 0.09) \times 10^{-3}$ M.

For the case of acetone, a more careful examination of the conversion time profiles is necessary to reveal significant differences between the direct UV photolysis and the UV/TiO_2 degradation routes. Although the photocatalytic reaction pathway is not as effective for the degradation of acetone as it is for isopropanol in aqueous solution, Fig. 1b shows that the direct photolysis route lags behind the former reaction in the later stages of the treatment. It is significant that at the initial pH of 8.62 and 4.11 the direct photochemical reaction levels off after 6 min while the photocatalytic reaction counterpart shows progressive acetone consumption through a first-order kinetic, as determined earlier in this paper.

Several competitive processes may cause the leveling off of the direct photolysis curves of acetone. According to early studies, the photolysis of acetone in solution proceeds via the excited $n{-}\pi^*$ triplet state with the formation of acetyl and methyl radicals by α-cleavage (Eq. (3)) (the species in aqueous solution denoted by the subscript “aq”) [48–51].

$$(CH_3COCH_3)_{aq} + h\nu \leftrightarrow \underset{\text{Solvent cage}}{(CH_3CO^{\cdot} + CH_3^{\cdot})_{aq}} \rightarrow CH_3CO^{\cdot}_{free} + CH^{\cdot}_{3\ free} \tag{3}$$

However, the quantum yield of acetone decomposition in water is low ($\Phi_{270nm} = 0.061$, [48]) due to the recombination of the radicals caused by the “cage” effect (Eq. (3)) or due to the deactivation of the active molecules by several pathways: (i) collision [50], (ii) solvent-assisted photoenolization involving a six-membered intermediate species, [51,52] and (iii) self-quenching by hydrogen abstraction from ground state acetone [52]. In the last two mechanisms the enol form of acetone undergoes ketonization and the original compound is reformed. In dilute aqueous solutions, however, the self-quenching pathway is only a minor primary process compared to (ii) [52].

Our results in Fig. 1b for the UV photolysis of acetone are in agreement with the reported competition between the fruitful pathway (right side of Eq. (3)) and the triplet state deactivation processes. The leveling off of the direct photolysis curves of acetone may indicate the offset to acetone UV photolysis caused by the deactivation processes that reform the ground state of the compound.

On the other hand, the observation of a slow degradation of acetone through the TiO_2-based photocatalytic reaction (Fig. 1b) does not imply that the kinetics of this process is not controlled by the TiO_2 surface phenomena. There are reasons to believe that direct

UV photolysis would be even less efficient to degrade acetone when the TiO_2 particles are present in the reaction solution.

First, TiO_2 absorbs at $\lambda \leqslant 388$ nm [53] and, therefore, the catalyst particles suspended in the aqueous media affect the fraction of light absorbed by acetone, which possesses a weak absorption band centered around 262 nm [45] and is present at low concentration (mM level) in our suspensions. This is directly related to the decrease in photon flow able to penetrate aqueous suspensions of TiO_2, as demonstrated by Yurdakal et al. [54]. Second, it is likely that the surface hydroxyl groups of TiO_2 participate in the deactivation of the triplet state of acetone. Using infrared and phosphorescence spectroscopy combined with isotopic labeling methods, Anpo [55] indicated that the triplet state of acetone associated to the surface hydroxyl groups of porous Vycor glass (PVG) underwent efficient radiationless deactivation through a similar photoenolization mechanism proposed by Porter and co-workers [51,52]. Therefore, it is possible that this additional mechanism of deactivation of the excited state of acetone takes place in the presence of TiO_2 catalyst, suppressing the direct photolysis degradation of acetone even more in the heterogeneous reaction systems.

In light of the above, the presence of TiO_2 may affect two important factors that determine the direct UV photolysis of acetone: the probability of the light absorption event, and the probability that the excited state proceeds to a chemical reaction. Therefore, it is reasonable to suggest that with the addition of the catalyst the consumption of our model compound proceeds dominantly by the heterogeneous photocatalytic route. Hence, the present authors believe that the differences observed in the heterogeneous photocatalytic rates at different pH conditions, which were discussed earlier, are controlled by the presence of the TiO_2 catalyst.

4. Conclusion

A simple interpretation on the grounds of the multisite model and the influence of pH on the surface behavior were successful to explain the observed results for the effect of pH on the degradation of SPOCs possessing hydrogen-bonding capabilities. This study suggests that substrates such as small aliphatic alcohols and ketones may adsorb to the TiO_2 catalyst in contact with their aqueous solution through the formation of hydrogen bonds with the surface hydroxyl groups.

In terms of the mechanistic aspects of the photocatalytic degradation of our model compounds, acetone and isopropanol, this is of great interest because the idea of these substrates being hydrogen bonded to the layer of hydroxyl groups opens up the possibility that the reaction with the photogenerated hydroxyl radicals occurs at the surface of titanium dioxide. Therefore, our hydrogen-bonding hypothesis challenges the common assumption that our model compounds do not adsorb to the surface sites and their oxidative pathways of degradation only occur via homogeneous-phase reaction with free hydroxyl radicals. Currently, with the emerging hypothesis that terminal bridging surface hydroxyl groups are the only hole traps and, therefore, the only source of $OH^{\cdot}$ radicals [42,56], the possibility of these reacting species desorbing into the finite thickness of a reaction volume in the proximity of the surface could be completely disregarded. If this emerging idea proves to be correct, then the hydrogen-bonding hypothesis presented in this study will help reconcile the apparent contradiction of inexistent desorbing surface hydroxyl radicals attacking substrates that are not believed to interact with the surface.

In terms of practical UV/TiO_2 applications, we have shown that both factors hydrogen donor/acceptor capacities and rate of hydroxyl radical production should be considered at the moment of determining the optimal conditions for the degradation of substrates such as acetone and isopropanol. For example, a substrate that possesses both hydrogen donor and acceptor capabilities does not have restrictions to adsorb to the surface because hydrogen-bonding sites are present in all the ranges of pHs. Therefore, its fastest degradation occurs at conditions where the rate of hydroxyl radical production is more favorable (i.e., alkaline pH). On the contrary, if a given substrate does not possess the dual hydrogen donor and acceptor capacities, its adsorption to the surface is restricted to the conditions where suitable hydrogen-bonding surface sites exist. As a result, the adsorption to the surface is the most determining factor on its degradation.

Acknowledgments

The authors are grateful to the National Aeronautics and Space Administration (NCC 5-586) for financial support. They also acknowledge the help of Eduardo Martínez, Ph.D. in the Department of Mathematics at the University of Oklahoma in writing the Mathematica program.

References

[1] R.I. Bickley, G. Munuera, F.S. Stone, J. Catal. 31 (1973) 398.
[2] R.I. Bickley, R.K.M. Jayanty, Faraday Discuss. Chem. Soc. 58 (1974) 194.
[3] D. Brinkley, T. Engel, J. Phys. Chem. B 102 (1998) 7596.
[4] C.-P. Chang, J.-N. Chen, M.-C. Lu, J. Chem. Technol. Biotechnol. 79 (2004) 1293.
[5] J.M. Coronado, S. Kataoka, I. Tejedor-Tejedor, M.A. Anderson, J. Catal. 219 (2003) 219.
[6] J.M. Coronado, M.E. Zorn, I. Tejedor-Tejedor, M.A. Anderson, Appl. Catal. B 43 (2003) 329.
[7] J. Cunningham, B. Hodnett, J. Chem. Soc. Faraday Trans. 177 (1981) 2777.
[8] M. El-Maazawi, A.N. Finken, A.B. Nair, V.H. Grassian, J. Catal. 191 (2000) 138.
[9] S. Hager, R. Bauer, Chemosphere 38 (1999) 1549.
[10] M.A. Henderson, J. Phys. Chem. B 108 (2004) 18932.
[11] D. Kozlov, D. Bavykin, E. Savinov, Catal. Lett. 86 (2003) 169.
[12] S.A. Larson, J.A. Widegren, J.L. Falconer, J. Catal. 157 (1995) 611.
[13] Y. Ohko, K. Hashimoto, A. Fujishima, J. Phys. Chem. A 101 (1997) 8057.
[14] J. Peral, D.F. Ollis, J. Catal. 136 (1992) 554.
[15] W. Xu, D. Raftery, J. Catal. 204 (2001) 110.
[16] W. Xu, D. Raftery, J. Phys. Chem. B 105 (2001) 4343.
[17] W. Xu, D. Raftery, J.S. Francisco, J. Phys. Chem. B 107 (2003) 4537.
[18] R.B. Cundall, R. Rudham, M.S. Salim, J. Chem. Soc. Faraday Trans. 1 72 (1976) 1642.
[19] J. Cunningham, S. Srijaranai, J. Photochem. Photobiol. A 43 (1988) 329.
[20] P.R. Harvey, R. Rudham, S. Ward, J. Chem. Soc. Faraday Trans. 179 (1983) 1381.
[21] Y. Kado, M. Atobe, T. Nonaka, Ultrason. Sonochem. 8 (2001) 69.
[22] P.A. Mandelbaum, A.E. Regazzoni, M.A. Blesa, S.A. Bilmes, J. Phys. Chem. B 103 (1999) 5505.
[23] M. Miyake, H. Yoneyama, H. Tamura, Chem. Lett. 5 (1976) 635.
[24] N. Sakaguchi, S. Matsuo, T. Kurisaki, T. Matsuo, H. Wakita, Res. Chem. Intermediat. 32 (2006) 95.
[25] S. Yamagata, S. Nakabayashi, K.M. Sancier, A. Fujishima, Bull. Chem. Soc. Jpn. 61 (1988) 3429.
[26] C.E. Verostko, B.W. Finger, B.E. Duffield, Design of a post-processor for a water recovery system, in: 30th International Conference on Environmental Systems (SAE Paper 2519), Toulouse, France, 10–13 July 2000.
[27] H.-W. Liu, C.-H. Wu, J.-G. Lo, in: D. Barceló (Ed.), The Handbook of Environmental Chemistry, vol. 5, Part I, Springer-Verlag, Berlin, Heidelberg, 2004, p. 29.
[28] K.S. Kim, M.A. Barteau, W.E. Farneth, Langmuir 4 (1988) 533.
[29] G. Munuera, F.S. Stone, Discuss. Faraday Soc. 52 (1971) 205.
[30] C.M. Hollabaugh, J.J. Chessick, J. Phys. Chem. 65 (1961) 109.
[31] Y. Suda, T. Morimoto, M. Nagao, Langmuir 3 (1987) 99.
[32] M. Mrowetz, E. Selli, Phys. Chem. Chem. Phys. 7 (2005) 1100.
[33] Y. Sun, J.J. Pignatello, Environ. Sci. Technol. 29 (1995) 2065.
[34] S. Tunesi, M. Anderson, J. Phys. Chem. 95 (1991) 3399.
[35] G. Riegel, J.R. Bolton, J. Phys. Chem. 99 (1995) 4215.
[36] M.H. Abraham, Chem. Soc. Rev. 22 (1993) 73.
[37] T. Hiemstra, J.C.M. De Wit, W.H. Van Riemsdijk, J. Colloid Interf. Sci. 133 (1989) 105.
[38] T. Hiemstra, W.H. Van Riemsdijk, G.H. Bolt, J. Colloid Interf. Sci. 133 (1989) 91.
[39] T. Hiemstra, W.H. Van Riemsdijk, Colloid. Surf. 59 (1991) 7.
[40] R. Rodríguez, M.A. Blesa, A.E. Regazzoni, J. Colloid Interf. Sci. 177 (1996) 122.
[41] H.P. Boehm, Discuss. Faraday Soc. 52 (1971) 264.
[42] P. Salvador, J. Phys. Chem. C 111 (2007) 17038.
[43] M. Stefan, A.R. Hoy, J.R. Bolton, Environ. Sci. Technol. 30 (1996) 2382.
[44] J.A.R. Van Veen, F.T.G. Veltmaat, G.A. Jonkers, J. Chem. Soc. Chem. Commun. 23 (1985) 1656.

[45] V. Feigenbrugel, C. Loew, S. Le Calvé, P. Mirabel, J. Photochem. Photobiol. A 174 (2005) 76.
[46] C. Von Sonntag, H.-P. Schuchmann, Adv. Photochem. 10 (1977) 59.
[47] L. Farkas, Y. Hirshberg, J. Am. Chem. Soc. 59 (1937) 2450.
[48] M. Anpo, Y. Kubokawa, Bull. Chem. Soc. Jpn. 50 (1977) 1913.
[49] J.C. Dalton, N.J. Turro, Ann. Rev. Phys. Chem. 21 (1970) 499.
[50] R. Pieck, E.W.R. Steacie, Can. J. Chem. 33 (1955) 1304.
[51] G. Porter, R.W. Yip, J.M. Dunston, A.J. Cessna, S.E. Sugamori, Trans. Faraday Soc. 67 (1971) 3149.
[52] G. Porter, S.K. Dogra, R.O. Loutfy, S.E. Sugamori, R.W. Yip, J. Chem. Soc. Faraday Trans. 169 (1973) 1462.
[53] H. De Lasa, B. Serrano, M. Salaices, Photocatalytic Reaction Engineering, Springer Science, New York, 2005.
[54] S. Yurdakal, V. Loddo, B.B. Ferrer, G. Palmisano, V. Augugliaro, J. Giménez Farreras, L. Palmisano, Ind. Eng. Chem. Res. 46 (2007) 7620.
[55] M. Anpo, Chem. Lett. 6 (1987) 1221.
[56] D. Monllor-Satoca, R. Gómez, M. González-Hidalgo, P. Salvador, Catal. Today 129 (2007) 247.