

## Research Article

# TiO<sub>2</sub> Nanoparticles-Photocatalytic Oxidation of Selected Cycloalkanols

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Received 26 July 2007; Accepted 20 December 2007

Recommended by Russell Howe

Photocatalytic oxidation of cyclohexanol (1), cyclopentanol (2), and cycloheptanol (3) was investigated by using titanium dioxide (Degussa P25) as a semiconductor photocatalyst. The effect of different operational parameters such as the catalyst, the solvent, time, and oxidant was also studied. Results showed a high percentage of conversion for 1–3 (71.6%, 94.2%, and 100%, resp.) and that the primary photocatalytic oxidation products are the corresponding cycloalkanones (4–6). They were formed with high selectivity (>85%). Several other products were also identified using GC, GC/MS techniques and authentic samples. The photocatalytic activity is explained by a photoinduced electron transfer mechanism through the formation of electron-hole pair at the surface of the semiconductor particles. A first-order kinetic model was observed for the photocatalytic oxidation of the investigated cycloalkanols.

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## 1. INTRODUCTION

Photocatalysis represents one of the promising technologies for photoenergy conversion started with the pioneer findings of Fujishima and Honda [1]. Its applications in water recycling, air-pollution treatment, as well as in organic synthesis have found a great interest [2–6].

There are many studies focused on the photocatalytic oxidation and degradation of several classes of organic compounds catalyzed by TiO<sub>2</sub> semiconductor particulates [7–13].

Photocatalytic oxidation and degradation of alcohols catalyzed by TiO<sub>2</sub> and other semiconductor particulates have found some interest. For example, Harvey et al. [14] studied photocatalytic oxidation of liquid propan-2-ol to propanone using suspensions of titanium dioxide irradiated with filtered UV radiation. The dependence of reaction rate on the square root of the intensity of the incident radiation, together with low quantum yields, reflects the dominance of photoelectron and photohole recombination within the TiO<sub>2</sub>. Cameron and Bocarsly [15] studied the photocatalytic oxidation of ethanol, benzyl alcohol, cinnamyl alcohol, n-hexyl alcohol, isopropyl alcohol, cyclopentanol, and cyclohexanol which

converted to the corresponding aldehyde or ketone by using oxygen gas and visible light 488 nm (85 mW) illumination from an Ar laser. The process was catalyzed by the presence of H<sub>2</sub>PtCl<sub>6</sub> and CuCl<sub>2</sub>.

Nishimoto et al. [16] studied the photocatalytic dehydrogenation of aliphatic alcohols by aqueous suspensions of platinized titanium dioxide, photoirradiation ( $\lambda_{\text{ex}} > 300$  nm) of Ar-purged aqueous propan-2-ol solution gave hydrogen and acetone. The regioselectivity in the semiconductor-mediated photooxidation of 1,4-pentanediol was studied in 1989 by Fox et al. [17].

We also studied the photocatalytic oxidation of selected aryl alcohols [18, 19]. The main oxidation products were the corresponding aldehydes or ketones and acids. Kinetic studies revealed a second-order reaction rate for benzyl alcohol as a model alcohol. Also photocatalytic oxidation of fluoren-9-ol and 4,5-diazafluoren-9-ol in nonaqueous oxygen saturated TiO<sub>2</sub> suspension to the corresponding ketones was formed in a high yield, in addition to minor amount of the corresponding hydrocarbon and other decomposition products. Interestingly, photocatalytic oxidation of the parent fluorene afforded fluorenone under the same conditions. Similarly, Phenyl-4-pyridylmethanols as an acyclic

simulant gave the corresponding ketone and hydrocarbon. Furthermore, the effect of solvent polarity has been tested [18, 19].

Pillai and Salhe-Demessie [20] studied the selective oxidation of primary and secondary aliphatic alcohols to their corresponding carbonyl compounds in gas phase. In 2006, Wu et al. [21] studied the long-term photocatalytic stability of  $\text{Co}^{2+}$ -modified P25- $\text{TiO}_2$  powders for the  $\text{H}_2$  production from aqueous ethanol solution. In this paper, the long-term stability of photocatalytic activity of  $\text{Co}^{2+}$  doped P25- $\text{TiO}_2$  nanoparticles for hydrogen production from aqueous ethanol solution was discussed in detail using a photoelectrochemical method.

It is clear from the previous survey that the effect of ring size and conditions on the photocatalytic oxidations of secondary cycloalkanols has not been tackled. So, this study will be of great interest.

## 2. EXPERIMENTAL

### 2.1. Materials

Titanium dioxide P25 (Degussa-Hüls AG, powder) was dried at  $120^\circ\text{C}$  for 24 hrs before use, these particles are composed mostly of anatase with surface area of  $37.7\text{ m}^2\text{g}^{-1}$ , average particle size 21 nm, and pore diameter 31.0. Oxygen was dried by passage through a drying calcium chloride tube. Acetonitrile and acetone (Sigma Aldrich, St. Louis, USA, HPLC grade) were distilled before use. Hydrogen peroxide was 30% (v/v). Cyclohexanol (1), cyclopentanol (2) and cycloheptanol (3) were purchased from Aldrich chemical company and were distilled before use. The authentic samples cyclohexanone (4), cyclopentanone (5), cycloheptanone (6), and 1,4-cyclohexadione (7) were obtained from Aldrich, whereas cyclohexyl formate (8) [22], 2-cyclohexenone (9) [23], 2-hydroxycyclohexanone (10) [24], n-hexanoic acid (11) [25], cyclohexyl hexanoate (12) [22], n-pentanoic acid (13) [22, 26], cyclopentyl pentanoate (14) [22], and n-heptanoic acid (15) [27] were synthesized as described in literatures. All the prepared authentic samples were analyzed by IR,  $^1\text{H-NMR}$ , GC, and GC/MS analyses as synthetic mixture.

### 2.2. Apparatus

A 450 W medium pressure mercury lamp (ACE glass, immersion type) with a pyrex well was used as the light source, which has a maximum emission range 296.7–578 nm (4.18 – 2.15 eV). The system was covered with aluminum foil which served as light reflector to decrease light loss and the apparatus was set up in a metallic cabinet. The distance between sample and irradiation source was 5 cm.

IR spectra were recorded using IR-470, IR spectrophotometer-Shimadzu using thin film and NaCl disks. The electronic absorption spectra were recorded using UV-2101 PC, UV-VIS scanning spectrophotometer-Shimadzu.  $^1\text{H-NMR}$  spectra were carried out using 90 MHz Varian 390 in  $\text{CDCl}_3$  and TMS as an internal standard. GC analy-

ses were performed employing Perkin Elmer, Autosystem XLGC using capillary column (5% diphenyl–95% dimethyl polysiloxane), length 30 m, internal diameter 0.32 mm, film thickness  $0.25\ \mu\text{m}$ . The initial temperature of column is  $40^\circ\text{C}$  and the final temperature is  $280^\circ\text{C}$ , the rate of heating is  $20^\circ\text{C}/\text{min}$ . The injector temperature is  $300^\circ\text{C}$  and the detector used is a flame ionization detector at  $250^\circ\text{C}$ . GC/MS analysis were carried out using GC model: GC 2000 thermo, capillary column DB-5 (5% phenyl–95% methyl polysiloxane, L. 30 m, I.D. 0.25 mm, F.T.  $0.25\ \mu\text{m}$ , temperature of column from  $50^\circ\text{C}$  to  $300^\circ\text{C}$ ,  $10^\circ\text{C}/\text{min}$ . and injector temperature  $250^\circ\text{C}$ ), attached with mass spectrometer: model SSQ 7000 produced by Finnigan. All melting points were determined on a Gallen-Kamp melting point apparatus.

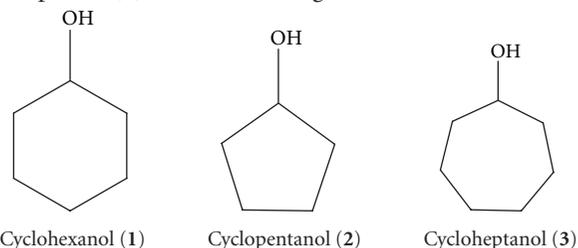
### 2.3. General procedure

A 75 ml (0.1 M) solution of the investigated cycloalkanols (1–3) was prepared in the used solvent, 75 mg of titanium dioxide (P25 Degussa-Hüls AG) was added to the solution, the mixture was transferred to the reaction vessel and sonicated in an ultrasonic bath for 15 minutes. The stirred suspension was bubbled with a stream of oxygen gas at a flow rate (30 ml/min) and then illuminated for 20 hours using 450 W medium pressure mercury lamp. The reaction progress was monitored by GC. After irradiation, the titanium dioxide powder was removed by filtration using a medium porosity frit and the solvent was evaporated by using rotatory evaporator. The reaction mixture was analyzed by using GC and GC/MS techniques, and then the products were identified and estimated with convincing match qualities compared with the standard mass spectra in the mass spectral libraries and with their retention time matched with authentic samples.

## 3. RESULTS AND DISCUSSIONS

Application of photocatalysis in our daily life and chemical industries has found a great interest. As reported in the introduction, the superior  $\text{TiO}_2$  photocatalyst was elegantly used for several photocatalytic oxidation processes. The present work is directed for synthesis, mechanistic, and selectivity studies as well as for decontamination purposes.

The target starting materials include three selected alicyclic alcohols; cyclohexanol (1), cyclopentanol (2), and cycloheptanol (3); of different ring sizes.



Results obtained in this work will be presented for each individual alcohol; and collective table and figures are also available in the following discussion.

### 3.1. PCO of cyclohexanol (1) and cyclohexanone (4)

#### 3.1.1. PCO of 1 in acetonitrile

After irradiation of **1** in dry acetonitrile, the photolysis product, using GC/MS technique, were cyclohexanone (**4**, 45.6%), 1,4-cyclohexanedione (**7**, 3.2%), cyclohexyl formate (**8**, 2.5%), 2-cyclohexenone (**9**, 1.8%), 2-hydroxycyclohexanone (**10**, 1.1%), n-hexanoic acid (**11**, 4.0%), 5-hexenal (**16**, 2.9%), 4-hydroxycyclohexanone (**17**, 4.4%), and cyclohexyl hexanoate (**12**, 3.0%), and other product (**19**, 2.9%) (Table 1, Exp. 1).

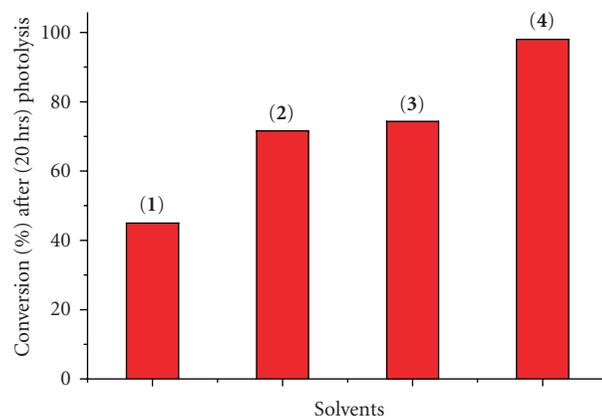
Cyclohexanol (**1**) is a sensitive probe, for it has been established that two electron oxidation will give cyclohexanone (**4**) [17] as a primary product, whereas single electron oxidation selectively produces the open-chain unsaturated aldehyde 5-hexenal (**16**) [17], also 5-hexenal (**16**) formed by intramolecular hydrogen transfer reaction of cyclohexanone. Cyclohexanone was also oxidized to n-hexanoic acid (**11**) [28, 29].

Cyclohexanone (**4**) can be hydroxylated by  $\cdot\text{OH}$  radical to 4-hydroxycyclohexanone (**17**) and 2-hydroxycyclohexanone (**10**). 1,4-cyclohexanedione (**7**) is most probably formed by oxidation of 4-hydroxycyclohexanone (**17**) [30] and 2-cyclohexenone (**9**) was probably formed by dehydration of 2-hydroxycyclohexanone (**10**) [14, 17], respectively. 3-hydroxycyclohexanone may be formed also, but not detected, and dehydrated to 2-cyclohexenone (**9**). This is because the heat of formation [31] of the three hydroxylated cyclohexanones are close to each other ( $-101.61$ ,  $-99.88$ ,  $-103.64$  Kcal/mol, resp.). This means that they are close in stability and probability of formation. 5-hexenal (**16**) oxidation by double bond cleavage to formaldehyde [32] which by further oxidation gives formic acid. Cyclohexanol (**1**) can react with formic acid to give cyclohexyl formate (**8**), and with n-hexanoic acid (**11**) to give cyclohexyl hexanoate (**12**), (Scheme 1).

#### 3.1.2. PCO of 1 in acetone:

After irradiation of **1** in acetone, the photolysis products analyzed by GC/MS technique were cyclohexanone (**4**, 25.2%), 1,4-cyclohexanedione (**7**, 3.4%) cyclohexyl formate (**8**, 2.3%), 2-hydroxycyclohexanone (**10**, 0.5%), n-hexanoic acid (**11**, 5.4%), 5-hexenal (**16**, 1.9%), and 4-hydroxycyclohexanone (**17**, 3.5%), 1,1'-bicyclohexyl-1,1'-diol (**18**, 2.5%) (Table 1, Exp. 4).

GC chromatogram and the suggested mechanism of these products showed that nearly all products formed in acetone are the same as the products formed in acetonitrile, but in lower conversion. From Table 1, the conversion of cyclohexanol (**1**) in dry acetonitrile was 71.6%, while in dry acetone equals to 45% (Figure 1). This is because the dielectric constant (DEC) of acetonitrile is much higher than that of acetone, 37.5 and 21.4, respectively [33]. A plausible explanation is that increase of solvent polarity increases the stabilization of the intermediate radical cations which in turn raise the percentage of the oxidation products [33].



- (1)  $(\text{CH}_3)_2\text{CO}$
- (2)  $\text{CH}_3\text{CN}$
- (3)  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  (4:1)
- (4)  $\text{CH}_3\text{CN}-30\% \text{H}_2\text{O}_2$  (4:1)

FIGURE 1: Effect of solvents on photocatalytic oxidation of cyclohexanol (**1**).

This supports the electron/hole mechanism in photocatalytic oxidation of the investigated alcohols.

#### 3.1.3. PCO of 1 in acetonitrile-water (4:1)

Irradiation products of **1** in acetonitrile-water mixture (4:1), as analyzed by GC/MS, were cyclohexanone (**4**, 39.7%), 1,4-cyclohexanedione (**7**, 3.7%), cyclohexyl formate (**8**, 1.43%), 2-cyclohexenone (**9**, 2.4%), 2-hydroxycyclohexanone (**10**, 7.8%), 5-hexenal (**16**, 1.8%), 4-hydroxycyclohexanone (**17**, 11.0%) and 1,4-cyclohexanediol (**20**, 6.5%), (Table 1, Exp. 2).

The products formed in aqueous acetonitrile are almost similar to those formed in acetonitrile, but the experimental conversion and yield distribution are different (Table 1). Conversion of **1** in aqueous acetonitrile (4:1) is 74.3% more than in dry acetonitrile (71.6%) this is because the dielectric constant (DEC) of water is 78.3 [34] (Figure 1). Also primary oxidant in this reaction is expected to be the strong oxidant  $\cdot\text{OH}$  radical generated by trapping a photohole at an adsorbed water molecule [35]. The percentage of hydroxylated compounds increased from 5.5% to 25.3%, and a new product is formed 1,4-cyclohexanediol (**20**).

#### 3.1.4. PCO of 1 in acetonitrile-30% $\text{H}_2\text{O}_2$ (4:1)

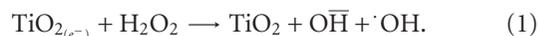
Irradiation of **1** in acetonitrile-30% hydrogen peroxide (4:1) without oxygen passage, using GC/MS analyses of the photolysate gave cyclohexanone (**4**, 13.6%), 1,4-cyclohexanedione (**7**, 8.7%), 2-cyclohexenone (**9**, 5.1%), 2-hydroxycyclohexanone (**10**, 10.2%), 4-hydroxycyclohexanone (**17**, 10.5%) and 1,4-cyclohexanediol (**20**, 8.2%), glutaric acid (**21**, 12.0%) and adipic acid (**22**, 29.8%) (Table 1, Exp. 3).

TABLE 1: Photocatalytic oxidation of the investigated cyclalkanols 1–3.

Exp.	Substrate	Solvents	Time (hrs)	Conv. (%)	Products (No, yield%)
1	Cyclohexanol (1)	CH <sub>3</sub> CN	20	71.6	Cyclohexanone (4, 45.6), 1,4-Cyclohexanedione (7, 3.2), Cyclohexyl formate (8, 2.5), 2-Cyclohexenone (9, 1.8), 2-Hydroxycyclohexanone (10, 1.1) n-Hexanoic acid (11, 4.0), Cyclohexyl hexanoate (12, 3.0), 5-Hexenal (16, 2.9), 4-Hydroxycyclohexanone (17, 4.4), Other product (19, 2.9).
2	Cyclohexanol (1)	CH <sub>3</sub> CN+H <sub>2</sub> O (4:1)	20	74.3	Cyclohexanone (4, 39.7), 1,4-Cyclohexadione (7, 3.7), Cyclohexyl formate (8, 1.4), 2-Cyclohexenone (9, 2.4), 2-Hydroxycyclohexanone (10, 7.8), 5-Hexenal (16, 1.8), 4-Hydroxycyclohexanone (17, 11.0), 1,4-Cyclohexanediol (20, 6.5).
3	Cyclohexanol (1)	CH <sub>3</sub> CN+H <sub>2</sub> O <sub>2</sub> (4:1)	20	98.0	Cyclohexanone (4, 13.6), 1,4-Cyclohexadione (7, 8.7), 2-Cyclohexenone (9, 5.1), 2-Hydroxycyclohexanone (10, 10.2), 4-Hydroxycyclohexanone (17, 10.5), 1,4-Cyclohexanediol (20, 8.2), Glutaric acid (21, 12.0), Adipic acid (22, 29.8).
4	Cyclohexanol (1)	H <sub>3</sub> COH <sub>3</sub>	20	45	Cyclohexanone (4, 25.2), 1,4-Cyclohexadione (7, 3.4), Cyclohexyl formate (8, 2.3), 2-Hydroxycyclohexanone (10, 0.5) n-Hexanoic acid (11, 5.4), 5-Hexenal (16, 1.9), 4-Hydroxycyclohexanone (17, 3.5), 1,1'-Bicyclohexyl-1,1'-diol (18, 2.5).
5	Cyclopentanol (2)	CH <sub>3</sub> CN	20	94.2	Cyclopentanone (5, 72.7), n-Pentanoic acid (13, 4.3), Cyclopentyl pentanoate (14, 2.8), 4-Pentalenal (23, 3.7), Other products (24, 3.1), (25, 5.8), (26, 1.8).
6	Cycloheptanol (3)	CH <sub>3</sub> CN	20	100	Cycloheptanone (6, 79.9), n-heptanoic acid (15, 3.2), 6-Heptenal (27, 1.8), 4-Hydroxycycloheptanone (28, 4.1), 1,4-Cycloheptadione (29, 4.7), 2-Hydroxycycloheptanone (30, 1.5).

GC chromatogram and the suggested mechanism of these products showed that most of products formed in acetonitrile-30% H<sub>2</sub>O<sub>2</sub> (4:1) mixture are the same as formed in dry acetonitrile with almost complete conversion of **1** (98%), that is, more than in dry acetonitrile or in aqueous acetonitrile (Figure 1). Electrons are donated from TiO<sub>2</sub> to hydrogen peroxide because it is a stronger oxidant than molecular oxygen [30]. When hydrogen peroxide accepts an electron, •OH radical may be produced according to (1) [35], so the •OH radicals are generated in large amounts, so the percentage of hydroxylated compounds increased, for example, the % of compound **10** increased from 1.1% to 7.8% to 10.2% in cases of acetonitrile, aqueous acetonitrile or acetonitrile-30% H<sub>2</sub>O<sub>2</sub>, respectively, and new

products were formed such as glutaric acid (**21**) and adipic acid (**22**).



The addition of H<sub>2</sub>O<sub>2</sub> is a well-known technique for increasing the rate of photocatalytic degradation with higher quantum yield of formation of •OH [30]. Consequently, the increased oxidation rate is expected by the addition of H<sub>2</sub>O<sub>2</sub> as shown in Table 1 (Exps. 1–3).

It is worthy to mention that no oxidation products could be detected with cyclohexanol in the absence of catalyst and/or light [30]. This is a good proof for the role of each parameter (H<sub>2</sub>O<sub>2</sub>, TiO<sub>2</sub> and light) in the photocatalytic oxidation process.

TABLE 2: Photocatalytic Oxidation of the Investigated Ketones 4–6:

Exp.	Substrate	Solvents	Time (hrs)	Conv. (%)	Products (No,%)
7	Cyclohexanone (4)	CH <sub>3</sub> CN	20	19.8	1,4-Cyclohexadione (7, 4.1), 2-Cyclohexenone (9, 1.4), 2-Hydroxycyclohexanone (10, 0.3) n-Hexanoic acid (11, 6.2), 5-Hexenal (16, 3.5), 4-Hydroxycyclohexanone (17, 3.8).
8	Cyclopentanone (5)	CH <sub>3</sub> CN	20	26.3	n-Pentanoic acid (13, 15.9), 4-Pentalal (23, 10.4).
9	Cycloheptanone (6)	CH <sub>3</sub> CN	20	29.9	n-heptanoic acid (15, 6.8), 6-Heptenal (27, 4.1), 4-Hydroxycycloheptanone (28, 7.8), 1,4-Cycloheptanedione (29, 7.8), 2-Hydroxycycloheptanone (30, 3.4).

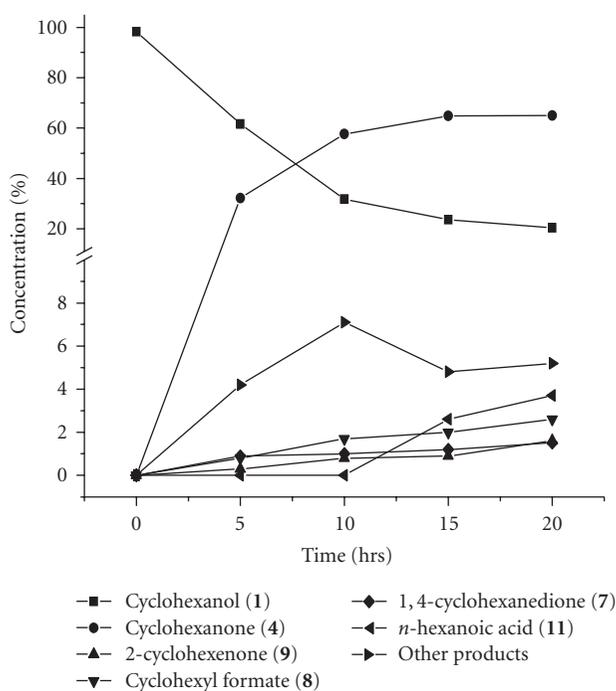


FIGURE 2: Photocatalytic Oxidation of cyclohexanol (1) in acetonitrile.

### 3.1.5. PCO of cyclohexanone (4) in acetonitrile

To shed more light on the formation and fate of the primary photooxidation products, cyclohexanone was irradiated at the same previous conditions. The conversion was only 19.8% after 20 hours irradiation. The GC/MS analyses of the photolysis products were 1,4-cyclohexanedione (7, 4.1%), 2-cyclohexenone (9, 1.4%), 2-hydroxycyclohexanone (10, 0.3%), n-hexanoic acid (11, 6.2%), 5-hexenal (16, 3.5%), and 4-hydroxycyclohexanone (17, 3.8%) (Table 2, Exp.7).

GC chromatogram and the suggested mechanism of these products matches those obtained from photocatalytic oxidation of cyclohexanol (1).

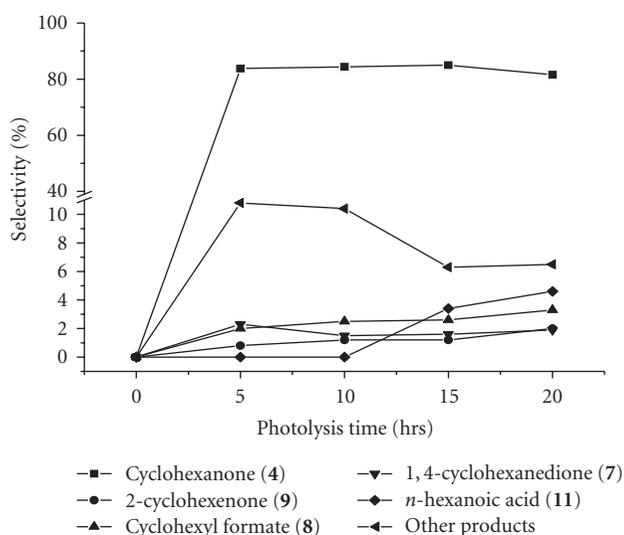


FIGURE 3: Selectivity of products of PCO of 1 in acetonitrile.

## 3.2. PCO of cyclopentanol (2) and cyclopentanone (5)

### 3.2.1. PCO of 2 in acetonitrile using TiO<sub>2</sub>

After irradiation of 2 in acetonitrile, the residue was analyzed by GC/MS. The photolysis products were cyclopentanone (5, 72.7%), n-pentanoic acid (13, 4.3%), cyclopentyl pentanoate (14, 2.8%), 4-pentalal (23, 3.7%), and some other unidentified low concentration products (24, 3.1%, 25, 5.8%, and 26, 1.8%) (Table 1, Exp. 5).

GC chromatogram and the suggested mechanism of these products showed that cyclopentanol (2) via two electron oxidation gave cyclopentanone (5) [17] as a primary product, whereas single electron oxidation selectively produces open chain unsaturated aldehyde 4-pentalal (23) [17]. Also 4-pentalal (23) may be formed by intramolecular hydrogen atom transfer reaction of cyclopentanone [28]. Cyclopentanone was also oxidized to n-pentanoic acid (13), which reacted with cyclopentanol (2) to give cyclopentyl pentanoate (14) (Scheme 2).

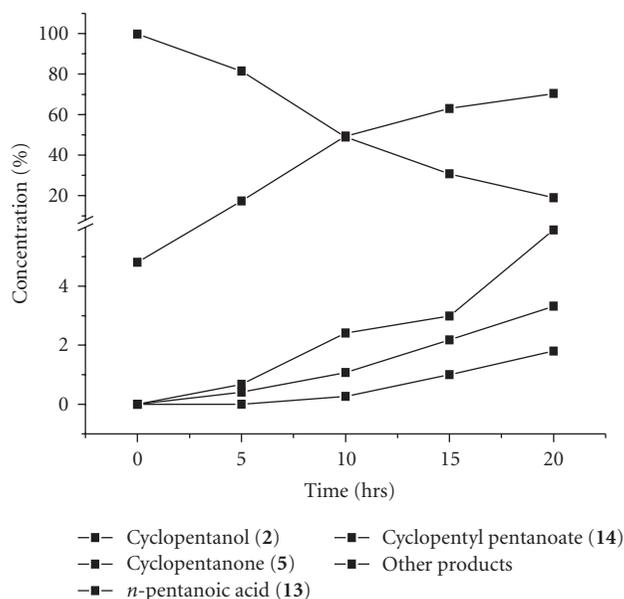


FIGURE 4: Photocatalytic oxidation of cyclopentanol 2 in acetonitrile.

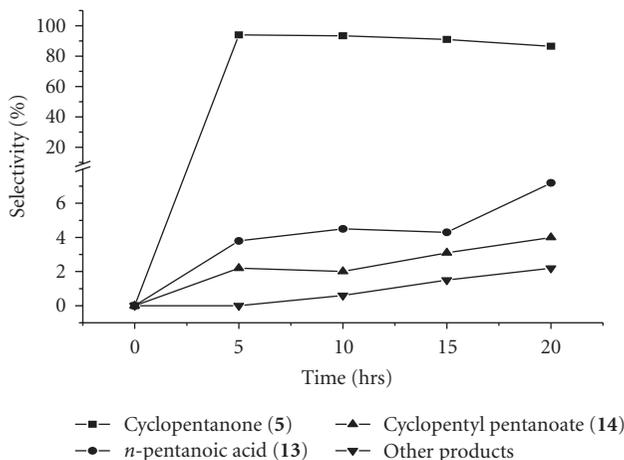


FIGURE 5: Selectivity of products of PCO of 2 in acetonitrile.

### 3.3.2. PCO of cyclopentanone (5) in acetonitrile

Great attention was focused on the oxidation of the primary oxidation product, cyclopentanone. Therefore, the photocatalytic oxidation of 5 under the same previous condition was investigated. Low conversion (26.3%) was observed and the photolysis products were n-pentanoic acid (13, 15.9%), and 4-pentenal (23, 10.4%) (Table 2, Exp. 8).

The suggested mechanism of these products is in agreement with the suggested mechanism of photocatalytic oxidation of cyclopentanol.

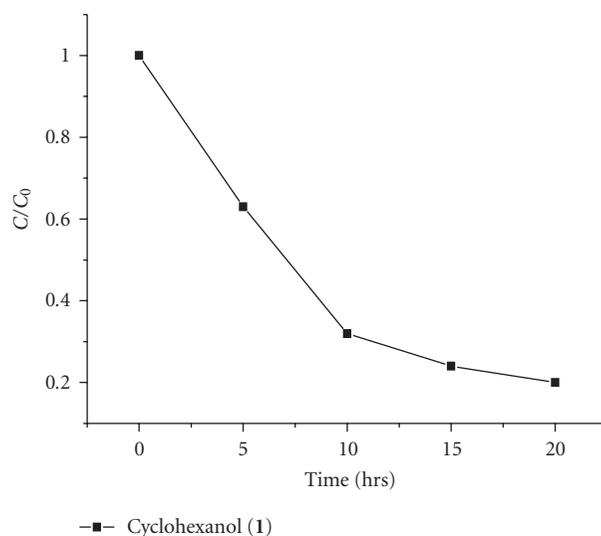


FIGURE 6: Photocatalytic disappearance of 1 in acetonitrile.

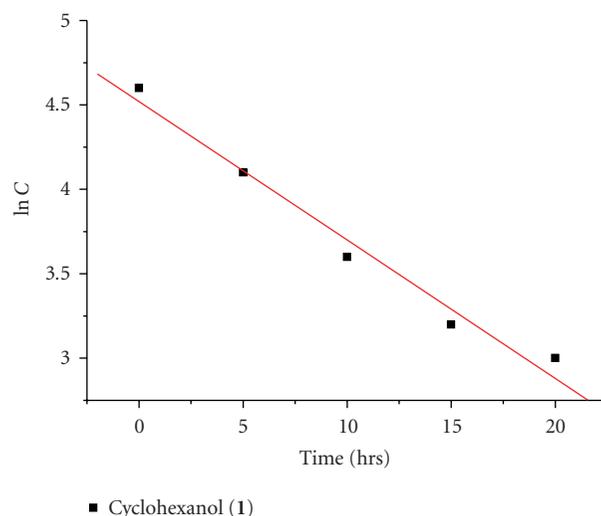


FIGURE 7: First-order PCO of 1 in acetonitrile ( $r = 0.9886$ ,  $k = -0.083 \text{ hr}^{-1}$ ).

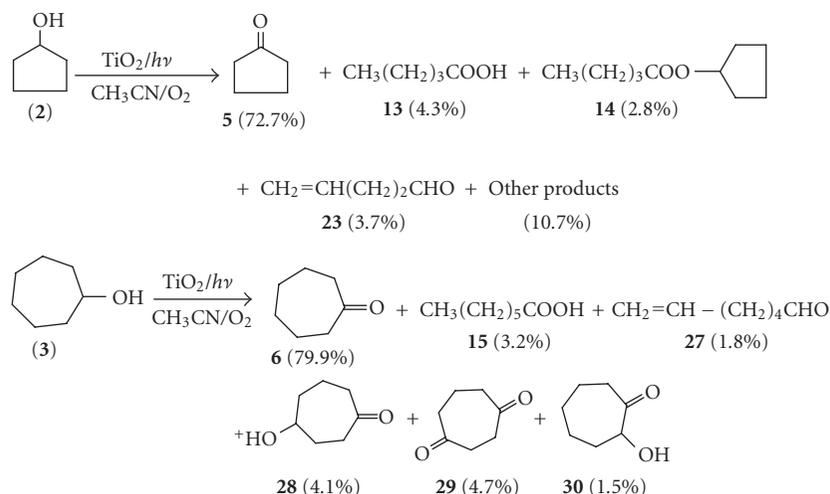
### 3.3. PCO of cycloheptanol (3) and cycloheptanone (6)

#### 3.3.1. PCO of 3 in acetonitrile using $\text{TiO}_2$

After irradiation of 3 in acetonitrile, the photolysis products, analyzed by GC/MS, were cycloheptanone (6, 79.9%), n-heptanoic acid (15, 3.2%), 6-heptenal (27, 1.8%), 4-hydroxycycloheptanone (28, 4.1%), 1,4-cycloheptadione (29, 4.7%) and 2-hydroxycycloheptanone (30, 1.5%) (Table 1, Exp. 6).

The suggested mechanism of these products showed that cycloheptanol (3) is a sensitive probe, therefore it has been established that two electron oxidation will give cycloheptanone (6) [17], whereas a single electron oxidation selectively produces the open-chain unsaturated





SCHEME 2: Photocatalytic oxidation of 2 and 3.

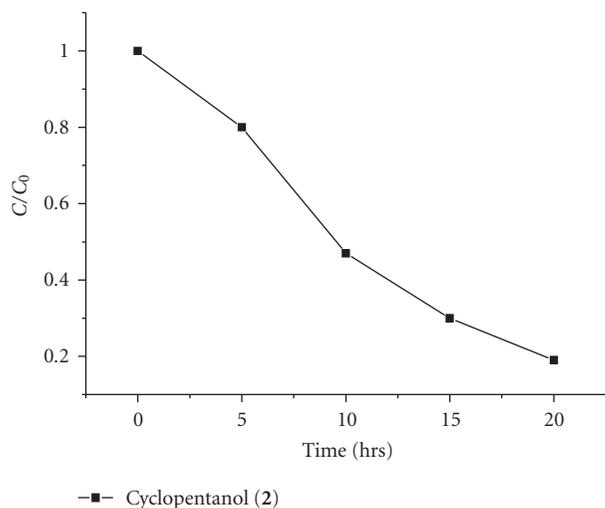


FIGURE 8: Photocatalytic disappearance of 2 in acetonitrile.

GC chromatogram and the suggested mechanism of these products are similar to the photocatalytic oxidation of cycloheptanol (3).

The obtained results indicated that the percentage conversion of 3 > 2 > 1, the same as that of corresponding ketones where 7 > 6 > 5. This is in agreement with their heat of formation ( $\Delta H_f = -60.83$ ,  $-66.98$ , and  $-80.22$  Kcal/mol, respectively). Of course cyclohexanol (1), the most stable one [31] ( $\Delta H_f = -80.22$  Kcal/mol), has the lowest percentage of conversion compared with 2 and 3.

#### 4. DISCUSSION

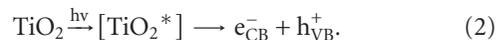
The main objectives of the present work include photocatalytic oxidation (PCO) of the selected alicyclic alcohols (1–3) of different ring sizes in the presence of aerated titanium dioxide (Degussa P25) suspensions in anhydrous acetonitrile and other solvent mixtures. A polar, nonhydroxylic solvent

(CH<sub>3</sub>CN) represents the best opportunity for controlling oxidative reactivity at the interface between a liquid reaction mixture and a solid irradiated photocatalyst [18, 19, 36]. To evaluate the role of each parameter in the system using cyclohexanol (1) as a model alcohol, we studied the effect of catalyst, light, oxygen, solvent polarity, and the effect of hydrogen peroxide as oxidizing agent instead of oxygen gas.

No oxidation products were detected upon irradiation of cyclohexanol (1) in the absence of catalyst and/or of light. Furthermore, experiments carried out in the absence of oxygen showed also no significant evidence of products formed. All these results confirm the essential role of oxygen, TiO<sub>2</sub> and light in the photocatalytic oxidation process [18, 19, 33].

Furthermore, the UV absorption spectra of the target compounds have been inspected to shed some light on their behavior upon irradiation. The maximum absorption of the investigated alcohols (1–3) ranges between 277.1 nm for 2 and 287.1 nm for 3, a range that will be cutoff by pyrex glass [18, 19]. As the maximum emission of the used 450 W medium pressure mercury lamp ranges between 296.7 nm–578.0 nm (4.18 – 2.15 eV), the obtained products are therefore originated through initial band gap excitation of TiO<sub>2</sub> (3.23 eV) [7, 37], but not through direct excitation of the alcohol.

In a photocatalytic process, the primary step following the radiation absorption by the photocatalyst is the generation of electron-hole pairs (2), which must be trapped in order to avoid recombination, that is, charge separation is essential for any photocatalytic electroprocess.



Despite the contributions from a number of research groups, detailed mechanisms of the photocatalytic oxidation processes at the TiO<sub>2</sub> surface remain elusive for many important organic materials particularly regarding the initial steps involved in the redox radical reactions, which may

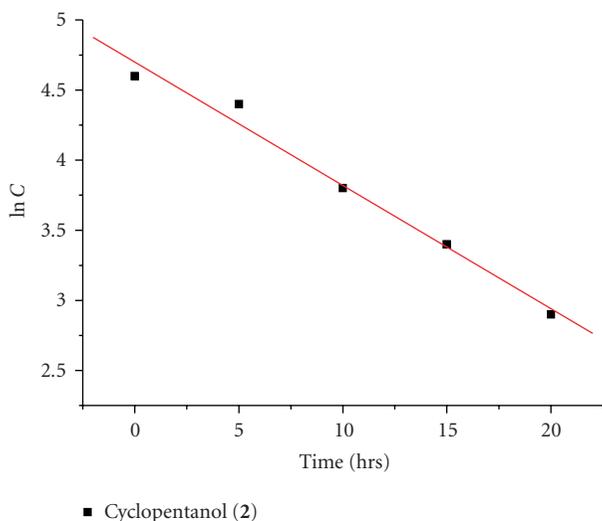
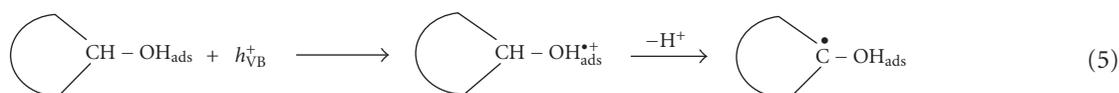


FIGURE 9: First-order PCO of 2 in acetonitrile ( $r = 0.9918$ ,  $k = -0.094 \text{ hr}^{-1}$ ).

involve one or more of the following radicals  $\text{O}_2^{\bullet-}$ ,  $\bullet\text{OH}$ ,  $\text{HOO}\bullet$ ,  $\text{Cl}\bullet$ , and so on. The use of nonaqueous reaction medium rules out the participation of hydroxy radicals generated by water trapping of the hole, in the oxidation process [38].

From the product distribution and reaction products profiles, the reaction mechanism of  $\text{TiO}_2$  sensitized photooxidation of the target alcohols (1–3) in aerated acetonitrile has been proposed.

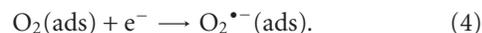
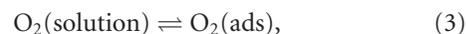


Two fates are available to such radical. (1) **A second electron oxidation:** the latter intermediate is extremely easily oxidized [17] by loss of a second electron generating a protonated carbonyl intermediate. This intermediate gives the proton to the environment forming the corresponding carbonyl compound (**two-electrons mechanism**). (2) **Trapping of  $\text{O}_2^{\bullet-}$  and/or  $\text{O}_2^{\bullet-}$ :** An alternative mechanism is the trapping of the  $\alpha$ -hydroxy radical by oxygen forming

The efficiency of the oxidation was governed by the oxidation potential of the alcohol, the availability of  $\alpha$ -hydrogens and the tightness of the association with the photocatalyst.

Cyclic voltammetric measurement using glassy carbon electrode revealed anodic oxidation potential of the model alcohol, cyclohexanol equals to (+0.85 V) which is less positive than the hole potential (+2.35 V), meaning that photocatalytic oxidation of cyclohexanol is thermodynamically possible. Also as the reduction potential of oxygen ( $-0.39 \text{ V}$ ) is less negative than the conduction band electron ( $-0.88 \text{ V}$ ), formation of the superoxide  $\text{O}_2^{\bullet-}$  is thermodynamically allowed in the reaction medium [18, 19, 33].

It is useful to stress on the point that in a photoreaction occurring on a semiconductor catalyst powder both the oxidation and reduction processes must occur on the same particle, although reaction sites for these processes may be different. Adsorbed oxygen species are the traps for electrons according to the following (3), (4), forming the radical anion  $\text{O}_2^{\bullet-}$  (superoxide).

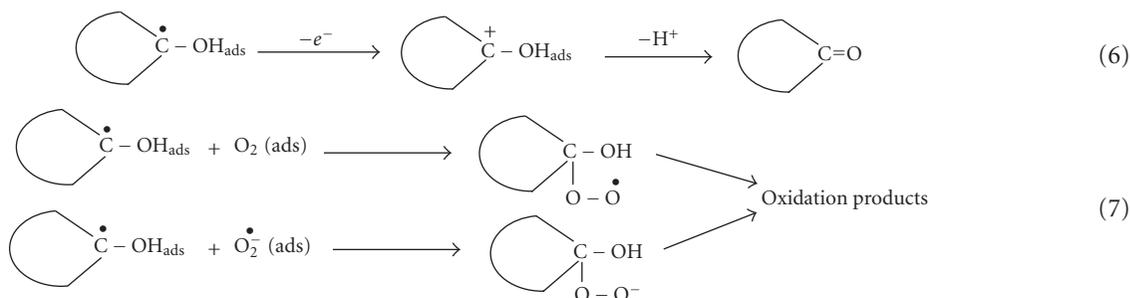


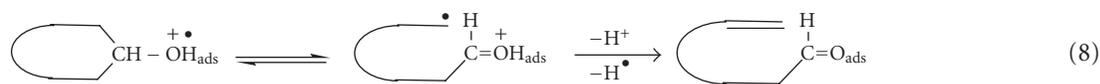
On the other hand, the adsorbed alcohol species in dry acetonitrile are the likely traps for holes forming the radical cation, by single electron transfer, which rapidly deprotonated producing  $\alpha$ -hydroxy radical of reasonable stability [17] as follows (5).

the peroxy radical or by superoxide ( $\text{O}_2^{\bullet-}$ ) forming peroxy anion, decomposition of which would be expected to occur rapidly to produce the carbonyl products [17] (6), (7).

Formation of the open-chain carbonyl compounds (8) can be produced by **ring rupture** of the  $\alpha$ -hydroxy radical cation [17] (**single-electron mechanism**).

These suggested mechanisms can be represented in general as follows:





Accordingly, the proposed photocatalytic oxidation (PCO) of cyclohexanol (1), for example, could be present as in Scheme 1. Also the PCO of 2 and 3 are summarized in Scheme 2.

## 5. KINETIC STUDIES

The photocatalytic oxidation reactions of cyclohexanol (1) and cyclopentanol (2) in acetonitrile were followed up by GC, as shown in Figures 2 and 4, respectively.

Selectivity of photocatalytic oxidation of cyclohexanol (1), cyclopentanol (2) are shown in Figures 3 and 5, respectively.

From these results, we can conclude that the photocatalytic oxidation of secondary alcohols 1, 2 have high selectivity to form ketones by more than 85%.

The kinetic disappearance [39] of the investigated alcohols (1, 2) from an initial concentration in acetonitrile was shown in Figures 6 and 8, respectively.

The semilogarithmic plots [39] of concentration data gave a straight line for cyclohexanol (1) and cyclopentanol (2) in acetonitrile as shown in Figures 7 and 9, respectively. These findings indicate that the photocatalytic oxidation of the investigated alcohols in  $\text{TiO}_2$  suspension can be described by the first-order kinetic model;  $\text{Ln}C = -kt + \text{Ln}C_0$ , where  $C_0$  is the initial concentration and  $C$  is the concentration of alcohols at time  $t$ . This is in agreement with the former work of Cinar on m-cresol [39].

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