

Photocatalytic oxidation of selected fluorenols on TiO₂ semiconductor

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Received 15 May 2002; accepted 24 May 2002

Abstract

Photocatalytic oxidation of the title compounds **1** and **2** in nonaqueous oxygen saturated TiO₂ suspension was carried out. The corresponding ketones were 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 (**3**) afforded fluorenone under the same conditions. Also, compound **4** as an acyclic simulant gave the corresponding ketone and hydrocarbon. Furthermore, the effect of solvent polarity has been tested.

An electron–hole pair generated on the irradiated TiO₂ surface is suggested for the semiconductor-mediated photocatalysis.
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Keywords: Photocatalytic oxidation; TiO₂; Fluorenols

1. Introduction

Photocatalysis of several classes of organic compounds using semiconductor particles under band gap irradiation as a little microreactors for the simultaneous reduction and oxidation of different redox system, has been intensively studied during the last 20 years, and several review articles have been recently published [1–8].

It appears to be the main focus of most of these studies is to investigate the principal applicability of photocatalytic systems for the efficient detoxification of water and air streams polluted with highly toxic chemicals [9–12].

Although a few compounds can undergo direct reactions when they are exposed to light, a wide range of other organic compounds can be destroyed in the photochemical processes. Photocatalytic processes can take place either in a homogenous medium containing a suitable additive (e.g. hydrogen peroxide) or in a colloidal (heterogeneous) suspension of semiconductor particles (e.g. titanium dioxide) [13].

Furthermore, several articles were appeared on the use of photocatalytic oxidation as a synthetic route for many organic compounds [5,12,14–17].

Continual interest in our laboratory on photocatalytic oxidation at irradiated semiconductors [18,19] inspired me to report here a recent investigation on irradiated fascinating

semiconductor, titanium dioxide (anatase), mediated photocatalytic oxidation of some representative polynuclear aromatic alcohols.

2. Experimental

2.1. Materials

Acetonitrile and acetone (Aldrich, HPLC grade) were distilled before use. Titanium dioxide (Aldrich, Anatase powder) was dried in an oven at 120 °C for 24 h and stored under nitrogen before use. Oxygen was dried by passage through a drying calcium chloride tube. Fluoren-9-ol (**1**), 4,5-diazafuoren-9-ol (**2**) and phenyl-4-pyridylmethanol (**4**) were prepared via literature procedures [20–22]. Fluorene (**3**) was commercially available (BDH) and recrystallized before use.

2.2. Apparatus

A 450 W medium pressure Hg lamp (ACE Glass, Immersion type) with a Pyrex well was used as the light source. The system was covered with aluminum foil which served as light reflector and the apparatus was set up in a metallic cabinet [18].

Melting points were measured on Mel-Temp. II melting point apparatus. IR spectra were done on Shimadzu-470 IR-Spectrophotometer using KBr-Wafer technique. UV spectra were performed using Shimadzu 2101 PC UV–Vis scanning spectrophotometer. ¹H NMR were carried out

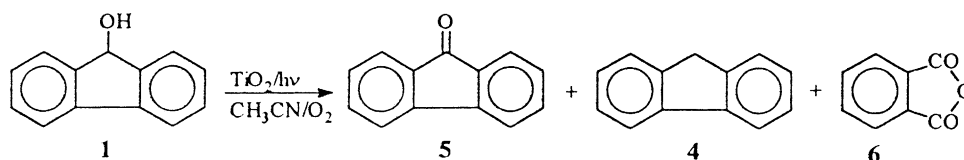
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using Varian EM-390, 90 MHz and a Jeol LA 400 MHz FT-NMR Spectrometer in CDCl_3 and DMSO using TMS as an internal standard. Elemental analyses were determined using Perkin-Elmer elemental analyzer 240C. TLC analyses were carried out using (40 mm \times 80 mm) and (20 cm \times 20 cm) precoated aluminum sheets covered with a thin film of silica gel with fluorescent indicator. GC/MS analyses were carried out on a Jeol TMS-600 H fitted with a Hewlett Packard gas chromatograph HP 6890 using HP-5 (cross-linked 5% PHME Siloxane) capillary column (30 m \times 0.35 mm \times 0.25 μm film thickness).

2.3. General procedure

A 400 ml solution (0.01 M) of the substrate (**1–4**) was prepared in dry acetonitrile (or acetone). TiO_2 (anatase, 100 mg)



was added to the solution and the mixture was transferred to the reaction vessel and sonicated in an ultrasonic bath for 15 min. The stirred suspension is bubbled with a slow stream of oxygen and then illuminated for the reaction period.

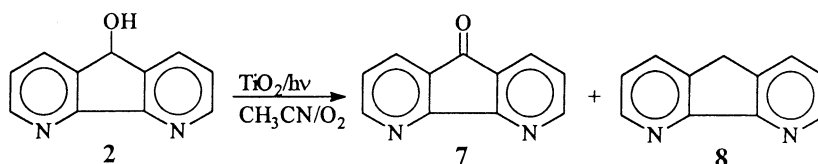
or acetone solutions of compounds **1–4** while purging with oxygen.

To verify the role of TiO_2 , light and oxygen in the oxidation process, blank tests of substrates **1–4** were carried under the same conditions, those used for the photocatalytic oxidation experiments. No oxidation products were detected in the absence of TiO_2 , O_2 and/or light. A very small amount of 9-fluorenone was formed from **1** in the presence of light only.

All direct photocatalytic oxidation of **1–4** gave mainly the corresponding ketones and alkanes in addition to small amount of the corresponding decomposition products. The products were assigned by comparison with authentic sample and/or by consideration of mass spectra data.

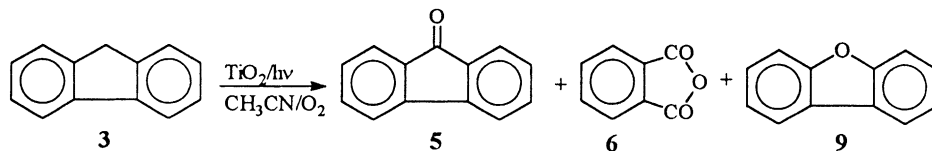
For example, photocatalytic oxidation of fluoren-9-ol (**1**) in acetonitrile or acetone gave fluoren-9-one (**5**, 86.8%/77.9%, M^+ at m/e 180) and fluorene (**4**, 7.6%/19.7%, M^+ at m/e 166) in addition to phthalic anhydride (**6**, 3.8%, M^+ at m/e 148) in case of acetonitrile.

Also, 4,5-diazafluoren-9-one (**7**, 71.4%, M^+ at m/e 182) and 4,5-diazafluorene (**8**, 8.8%, M^+ at m/e 168) in addition to minor unknown products were formed upon oxidation of 4,5-diazafluoren-9-ol (**2**).



The reaction process was monitored by TLC. After irradiation the color of the solution turned pale yellow. 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 using TLC and GC/MS techniques. Chemical yield of all products were determined by GC/MS analyses. Results are presented in Table 2.

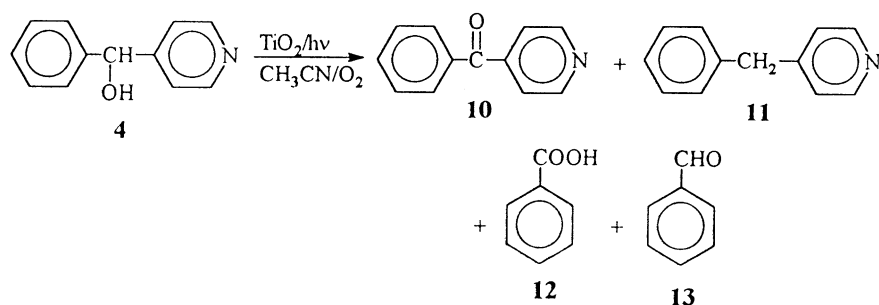
Interestingly, 9-fluorenone (**5**, 36.5%/30.5%) and dibenzofuran (**9**, 1.3%/1.0%, M^+ at m/e 168) were obtained from fluorene (**3**) upon photocatalytic oxidation in acetonitrile or acetone due to oxidation of the readily oxidizable methylene group. Phthalic anhydride was detected only in acetonitrile (**6**, 3.8%).



3. Results and discussion

The present work embraces a band gap irradiation of titanium dioxide (anatase) suspension in anhydrous acetonitrile

Furthermore, the photocatalytic oxidation of the acyclic simulant phenyl-4-pyridylmethanol (**4**) gave phenyl-4-pyridylketone (**10**, 82.1%, M^+ at m/e 183) as a major product, in addition to phenyl-4-pyridylmethane (**11**, 3.3%, M^+ at m/e 169), benzoic acid (**12**, 8.3%, M^+ at m/e 122) and benzaldehyde (**13**, 2.5%, M^+ at m/e 106).



The formation of benzaldehyde, benzoic acid, phthalic anhydride and dibenzofuran was confirmed from the mass spectral fragmentation as well authentic samples.

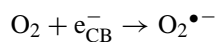
It was observed from Table 1 that the maximum absorption of the target compounds 1–4 ranges from 212.9 nm (3) to 289.8 nm, a range that will be cut off by Pyrex glass. The maximum emission of the 450 W medium pressure mercury lamp used in this study appears to be in the ranges 296.7–578.0 nm (4.18–2.15 eV).

Light absorption of energy equal to or greater than the band gap energy of TiO_2 (i.e. 3.23 eV) will result in electron ejection from the valence band to the conduction band generating a reactive electron ($E = -0.88$ V) and a positive hole ($E = 2.35$ V) [18,23,24]:



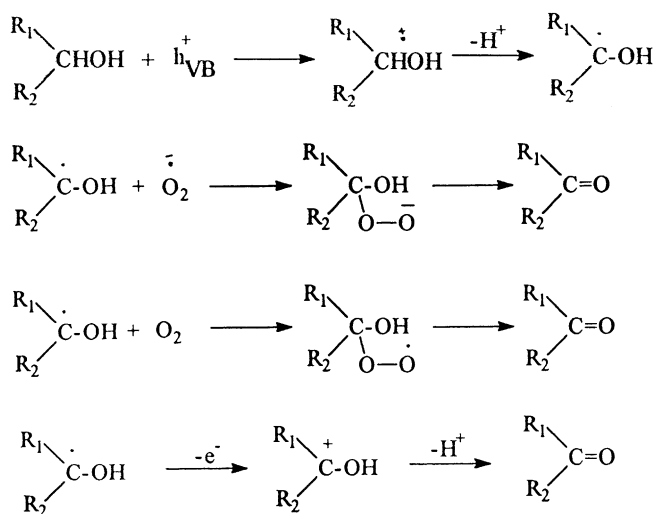
Accordingly, the electron–hole generation can be proposed to describe the result compounds in Table 2 [25,26].

The photogenerated electron can be trapped by adsorbed oxygen to form superoxide or other negatively charged adsorbed oxygen species:



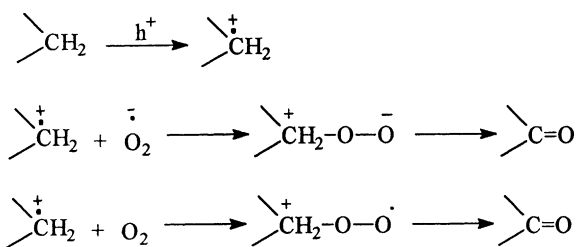
As the oxidizing power of the hole (+2.4 V vs. SCE in acetonitrile) is capable of initiating single electron oxidation of an adsorbed alcohol, the alcohol radical cation can be formed which rapidly deprotonated to the α -hydroxy radical. The radical intermediate is easily oxidized with

the photogenerated superoxide or even with oxygen as follows:



Photocatalytic oxidation of methylene group of compound

3 to carbonyl one is a result of the formation, $\text{>CH}_2^{\bullet +}$ via electron–hole transfer, which in turn reacts with the superoxide or with oxygen [18]. The same mechanism was suggested by Liang and Liu [27] to account for photocatalytic oxidation of diphenylmethane, by Ibusuki and Takeuchi [28] for photocatalytic oxidation of toluene and by Fox et al. [29] in the case of naphthalenes.



Investigation of the solvent effect on the photocatalytic oxidation of 9-fluorenone and fluorene has been carried out under the same photocatalytic conditions (Table 2). According to these results, the yield of ketone was decreased with decreasing the solvent polarity. For example, fluorenone (5) was obtained in 86.9 and 77.9% upon photocatalytic

Table 1
UV absorption of compounds 1–4

No.	Compound	λ_{max} (nm)	Absorbance (ϵ)
1	Fluorene-9-ol	270.50	2.610
		239.00	2.818
2	4,5-Diazafluorene-9-ol	258.20	1.300
		215.60	2.500
3	Fluorene	289.80	0.875
		279.80	0.639
		261.00	1.953
		212.90	1.973
4	Phenyl-4-pyridylmethanol	257.00	2.682
		230.80	2.800

Table 2
Photocatalytic oxidation products of compounds 1–4

No.	Substrate	Solvent	Time (h)	Conversion (%)	Products		
					Ketones (%)	Hydrocarbon (%)	Acids or aldehydes (%)
1	Fluoren-9-ol	CH ₃ CN	1.5	98.2	Fluoren-9-one (86.8)	Fluorene (7.6)	Phthalic anhydride (3.8)
		(CH ₃) ₂ CO	1.5	97.7	Fluoren-9-one (77.9)	Fluorene (19.7)	–
2	4,5-Diazafluoren-9-ol	CH ₃ CN	6	94.9	4,5-Diazafluoren-9-one (71.4) ^a	4,5-Diazafluorene (8.8)	–
3	Fluorene	CH ₃ CN	10	41.6	Fluoren-9-one (36.5) ^b	–	Phthalic anhydride (3.8)
		(CH ₃) ₂ CO	10	31.5	Fluoren-9-one (30.5) ^c	–	–
4	Phenyl-4-pyridylmethanol	CH ₃ CN	6	96.1	Phenyl-4-pyridylketone (82.1)	Phenyl-4-pyridyl-methane (3.3)	Benzoic acid (8.3)
							Benzaldehyde (2.5)

^a Other minor product [*m/e* 179 (5.7%), *m/e* 167 (9.0%), *m/e* 164 (5.1%)].

^b Dibenzofuran 1.3.

^c Dibenzofuran 1.0%.

oxidation of fluoren-9-ol (1) in acetonitrile (DEC = 37.5) and in acetone (DEC = 21.4), respectively.

A possible explanation is that increase of solvent polarity increases the stabilization of the intermediate radical ions which in turn raise the percentage of the product ketone [27].

Acknowledgements

The author would like to thank Prof. Dr. A.A. Abdel-Wahab for his kind help.

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