CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102779

Visible-Light-Induced Selective Photocatalytic Aerobic Oxidation of Amines into Imines on TiO_2

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Abstract: Imines are important intermediates for the synthesis of fine chemicals, pharmaceuticals, and agricultural chemicals. Selective oxidation of amines into their corresponding imines with dioxygen is one of the most-fundamental chemical transformations. Herein, we report the oxidation of a series of benzylic amines into their corresponding imines with atmospheric dioxygen as the oxidant on a surface of anatase TiO_2 under visible-light irradiation ($\lambda > 420$ nm). The visible-light response of this system was caused by the formation of a surface complex through the adsorption of a benzylic amine onto the surface of TiO_2. From the analysis of products of specially designed benzylic amines, we demonstrated that a highly selective oxygenation reaction proceeds via an oxygen-transfer mechanism to afford the corresponding carbonyl compound, whose further condensation with an amine would generate the final imine product. We found that when primary benzylic amines (13 examples), were chosen as the substrates, moderate to excellent selectivities for the imine products were achieved (ca. 38–94 %) in moderate to excellent conversion rates (ca. 44–95 %). When secondary benzylic amines (15 examples) were chosen as the substrates, both the corresponding imines and aldehydes were detected as the main products with moderate to high conversion rates (ca. 18–100 %) and lower selectivities for the imine products (ca. 14–69 %). When tribenzylamine was chosen as the substrate, imine (27 %), dibenzylamine (24 %), and benzaldehyde products (39 %) were obtained in a conversion of 50 %. This report can be viewed as a prototypical system for the activation of C−H bonds adjacent to heteroatoms such as N, O, and S atoms, and oxofuctionalization with air or dioxygen as the terminal oxidant under visible-light irradiation using TiO_2 as the photocatalyst.

Keywords: amines · charge transfer · imines · oxidation · photocatalysis · titanium

Introduction

TiO_2 is one of the most-attractive photocatalytic materials owing to its low cost, excellent chemical and photochemical stability, and nontoxicity.[1] However, because the band gap of TiO_2 is 3.2 eV (anatase), the TiO_2 photocatalyst can only be activated by UV-light irradiation ($\lambda < 385$ nm). To utilize the visible range of the solar spectrum, bulk doping with nonmetals such as H, B, C, N, and S atoms have attracted much attention.[2] However, such doping sites could act as recombination centers for the photoexcited charge-carriers. Thus, the visible-light activities of those TiO_2-based photocatalysts are relatively low. They are typically used for the degradation of very dilute pollutants and are not effective enough to perform organic syntheses at higher concentrations under visible-light irradiation.

Over the last few years, many efforts have been devoted to organic redox-transformation reactions using TiO_2 photocatalysis.[3] However, to date, most of the reported reactions for the synthetic transformations using TiO_2 photocatalysts were carried out under UV irradiation and were usually associated with low selectivity.[4] Performing visible-light-induced selective transformations by photocatalysts is a challenge that has attracted much attention, as shown by some special homogenous and heterogeneous systems.[5] Recent discoveries demonstrated that surface modification of TiO_2 with noble-metal complexes or nanoparticles rather than bulk doping might be a better strategy in the pursuit of new visible-light-responsive photocatalysts that could prompt the design of efficient redox reactions under visible-light irradiation. In particular, ruthenium-containing dyes[6] and gold nanoparticles[7] supported on TiO_2 have been successfully used for the reduction of nitrobenzene and the oxidation of alcohols under visible-light irradiation. However, to drive a photoredox reaction with a noble-metal-free organic dye as the antenna molecule is more appealing, provided that the dye is resilient under the photocatalytic conditions.

Indeed, we successfully used a commercially available dye, alizarin red, as the antenna molecule to absorb visible

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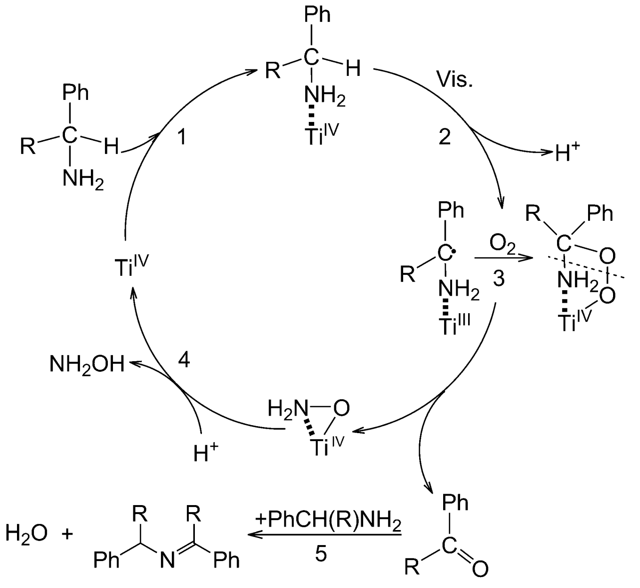
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102779.

light and drive the redox cycle of 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) to realize the oxidation of alcohols into their corresponding carbonyl compounds.[8] TEMPO is essential in the system to prevent degradation of the dye[9] and autooxidation of the substrates. However, this system is limited in substrate scope because TEMPO is only an efficient co-catalyst for the oxidation of alcohols. If the substrates themselves could act as the antenna to absorb visible light, the assembly could be simplified significantly. However, in general, organic substrates do not absorb visible light. Hence, they cannot play the role of the antenna molecule to initiate visible-light reactions directly. However, some colorless substrates adsorbed onto TiO_2 would form a surface complex that could absorb visible light and so initiate electron-transfer and the ensuing reactions.[10] This property can be further explored to achieve a more-straightforward solution for visible-light-induced organic transformations.

Recently, we discovered that oxygen transfer from dioxygen to the substrates dominates the aerobic oxidation of alcohols[11] and amines[12] on a TiO_2 surface in inert organic solvents under UV irradiation to afford high selectivities for the target products. The unique reaction of electrons in the conduction band of TiO_2 plays a dual role of activating the dioxygen and preventing the unselective autooxidation process. Merging these new discoveries into one unified photocatalytic system would be a powerful approach for highly selective oxidation reactions under visible-light irradiation; i.e., under visible-light irradiation, the photoinduced charge-transfer of the surface complex formed by adsorption of the substrates onto a TiO_2 surface would produce an oxidized substrate radical and an electron in the conduction band of TiO_2, whereas the unique reaction of an electron in the conduction band guarantees a high selectivity for the oxidation reaction.

Imines are important intermediates for the synthesis of fine chemicals, pharmaceuticals, and agricultural chemicals.[13] Herein, we report the oxidation of a series of benzylic amines into their corresponding imines using atmosphere dioxygen as the oxidant on TiO_2 under visible-light irradiation ($\lambda > 420$ nm). We envisage that this highly selective formation of imines under visible-light irradiation follows the mechanism in Scheme 1. The adsorption of benzylamine on TiO_2 would form a surface complex,[14] which plays the role of the antenna to absorb visible light (step 1). Upon visible-light irradiation, separation of the photogenerated charges occurs, the holes localize on the oxidized substrate, and electrons localize within the TiO_2 lattice. The deprotonation of the oxidized substrate generates a neutral carbon-centered radical (step 2). After that, the reaction mechanism should follow the same path as that under UV irradiation to produce the aldehyde. The interaction between dioxygen and the photogenerated free-radical and the electron in the conduction band of TiO_2 will finish the electron-transfer between the dioxygen and the substrate radical and the titanium(III) center (step 3).[11,12] The regeneration of the surface titanium(VI) sites of TiO_2 completes the photocatalytic oxidation cycle (step 4). The nucleophilic attack on such nascent aldehydes by the unreacted amines will thus yield the corresponding imines (step 5). The photoreaction process does not involve the hole in the valence band of TiO_2, which will help us to further reveal or confirm the mode of activation and the reaction of dioxygen on the TiO_2 surface.



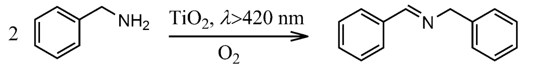
Scheme 1. Proposed mechanism for the formation of imines by the oxidation of amines on a TiO_2 surface under visible-light irradiation.

Results and Discussion

To test our hypothesis, benzylamine was chosen as the probe substrate to carry out the reaction (Table 1). First, we investigated whether there was visible-light absorption after the adsorption of benzylamine on the surface of anatase TiO_2, a prerequisite for a visible-light-induced reaction. From the UV/Vis spectra (Figure 1), we found that the adsorption of benzylamine onto the surface of TiO_2 extended the absorption spectrum of TiO_2 into the visible-light range, which provides the possibility of selective oxidation of benzylamine into an imine with dioxygen under $\lambda > 420$ nm irradiation (Table 1).

In control experiments, the reaction did not proceed without a photocatalyst (Table 1, entry 1), dioxygen (Table 1, entry 2), or visible-light irradiation (Table 1, entry 3). With 1 atm of air as the oxidant, TiO_2 as the photocatalyst, CH_3CN as the solvent, and irradiation at $\lambda > 420$ nm, the reaction proceeded smoothly to form the imine product with high selectivity (98 %) and a conversion of 54 % (Table 1, entry 4). With 2 atm of pure dioxygen as the oxidant, the reaction rate accelerated slightly (Table 1, entry 5) without having any influence on the selectivity. As atmospheric dioxygen is the best and most abundant oxidant, all of the following reactions were carried out in 1 atm air as the oxidant unless otherwise stated.

Table 1. The photocatalytic oxidation of benzylamine into an imine with dioxygen on a TiO_2 surface under visible-light irradiation.[a]



(1)

Entry	Photocatalyst	Solvent	Conv. [mol %][b]	Select. [mol %][b]
1	–	CH_3CN	0	–
2	TiO_2[c]	CH_3CN	0	–
3	TiO_2[d]	CH_3CN	0	–
4	TiO_2	CH_3CN	54	98
5	TiO_2[e]	CH_3CN	76	98
6	TiO_2 (P25)[f]	CH_3CN	35	98
7	TiO_2 (600 °C)[g]	CH_3CN	38	98
8	TiO_2 (700 °C)[g]	CH_3CN	18	98
9	TiO_2 (F)[g]	CH_3CN	43	98
10	TiO_2	CH_2Cl_2	38	97
11	TiO_2	DMF	35	97
12	TiO_2	$PhCH_3$	45	98
13	TiO_2	EtOAc	52	94
14	TiO_2	BTF	42	98

[a] Reaction conditions: benzylamine (0.2 mmol), solvent (5 mL), air (1 atm), TiO_2 (anatase, 50 mg; Alfa Aesar, $130\,m^2g^{-1}$), 4 h, Xe lamp (300 W, cutoff wavelengths below 420 nm). [b] Determined by GC analysis using bromobenzene as the internal standard. [c] Under an Ar atmosphere (1 atm). [d] 40 °C thermal reaction without irradiation. [e] O_2 (2 atm). [f] Degussa P25. [g] Calcinated at the respective temperatures or by treatment of hydrofluoric acid (see the Supporting Information). CH_3CN = acetonitrile, DMF = *N*,*N*-dimethylformamide, $PhCH_3$ = toluene, EtOAc = ethyl acetate, BTF = trifluorotoluene.

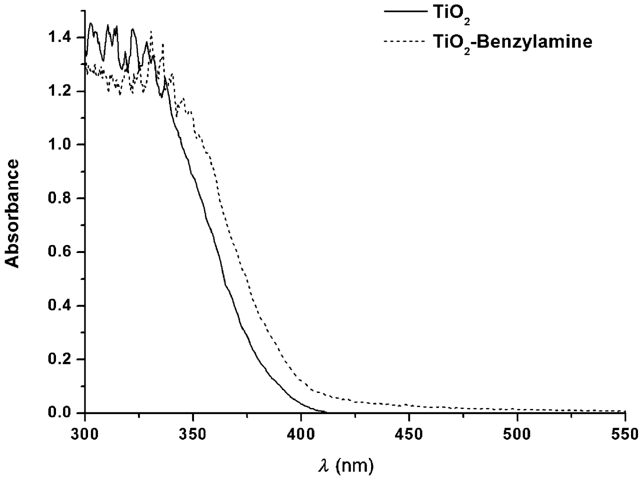


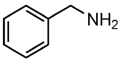
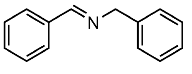
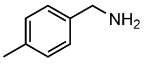
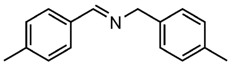
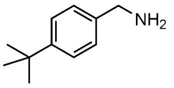
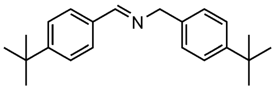
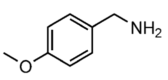
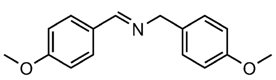
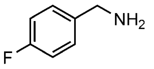
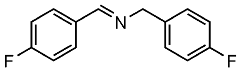
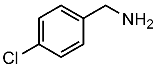
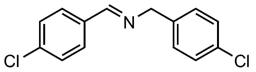
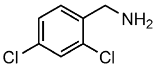
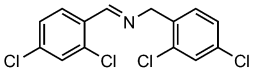
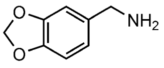
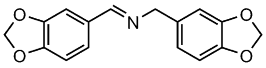
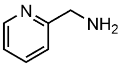
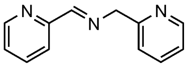
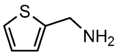
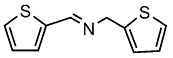
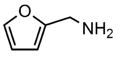
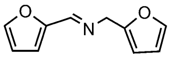
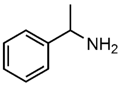
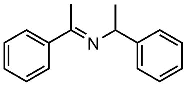
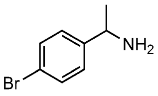
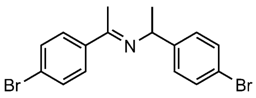
Figure 1. Adsorption spectra of TiO_2 and benzylamine adsorbed onto a TiO_2 surface (for experimental details, see the Supporting Information).

The photocatalytic activities of Degussa P25 TiO_2 and different calcined TiO_2 samples were also investigated (Table 1, entries 6–8). Degussa P25 TiO_2 usually has the highest activity for reactions under UV irradiation. However, the reaction rates in this reaction were in the order $TiO_2 > TiO_2$ (600 °C) $> TiO_2$ (Degussa P25) $> TiO_2$ (700 °C), which correlates well with the surface areas of these photocatalysts (see the Supporting Information, Table S1). However, treatment of the surface of TiO_2 with hydrofluoric acid to partially occupy the interaction sites of TiO_2 led to a decease in the reaction rate (Table 1, entry 9); this result indicates that the formation of a surface complex is essential for the photoreaction to proceed under visible-light irradiation. The influence of the solvent on the reaction was also investigated (Table 1, entries 4, 10–14). The reaction proceeded well in all of the inert organic solvents examined with little influence on the selectivity. The solvent did show an influence on the rate of reaction, and CH_3CN was found to be the best solvent among those examined. According to our proposed mechanism (Scheme 1), a condensation reaction (step 5) takes place to afford the imine. Thus, the polarity of CH_3CN should contribute to the formation of the imine. Note that DMF is the most polar solvent but competitive adsorption between the solvent and the substrate might result in the sluggish conversion rate observed (Table 1, entry 11).

Based on the preliminary results summarized in Table 1, we are quite optimistic about improving the efficiency of this photocatalysis reaction, by, for example, using anatase TiO_2 that has an even-larger surface area as the photocatalyst, using dioxygen to replace atmospheric air as the terminal oxidant, using other wide-band-gap metal-oxide semiconductors that have more-negative conduction bands than anatase TiO_2 as the photocatalyst, surface modification of the photocatalyst, etc.

To demonstrate the scope of this system, the photocatalytic oxidation of a variety of amine substrates was investigated. The results of the oxidation of various primary benzylic amines on a TiO_2 surface with 1 atm air in CH_3CN under visible-light irradiation ($\lambda > 420$ nm) are summarized in Table 2. The oxidation of benzylamine and its derivatives proceeded efficiently under visible-light irradiation with high conversion and high selectivity of their corresponding imines (Table 2, entries 1–7). The substituents on the benzene ring had a slight influence on the reaction rate and only a small influence on selectivity. The relatively low selectivity for the oxidation of 3,4-(methylenedioxy)benzylamine (Table 2, entry 8) into its corresponding imines might be caused by the activation of the substituents and an ensuing degradation process under these photocatalytic conditions. This system can tolerate the presence of heteroatoms (such as O, S, and N) on the aromatic ring (Table 2, entries 9–11), which often have detrimental effects on the activity of metal-complex catalysts, although a slight drop in selectivity was observed in comparison with those substrates without heteroatoms in the aromatic ring (Table 2, entries 1–7). When 1-phenylethylamine and its derivative were tested in the oxidation reaction (Table 2, entries 12 and 13), moderate selectivities for the corresponding imines were achieved with the formation of small amounts of corresponding acetophenone byproducts, thus suggesting that the oxygen-transfer from dioxygen to the substrates occurs as predicted (Scheme 1). The relatively low selectivity for the imine when 1-phenylethylamine and its derivatives were used as the substrates can be partially ascribed to the relative difficulty of the condensation reaction between the newly generated acetophenones and 1-phenylethylamine. As a result, for those substrates, only moderate selectivities

Table 2. Aerobic oxidation of primary benzylic amines photocatalyzed by TiO_2 under visible-light irradiation.[a]

Entry	Substrate	Product	t [h]	Conv. [mol %][b]	Select. [mol %][c]
1			10	91	92
2			6	78	94
3			10	90	94
4			5.5	95	93
5			6.5	84	88
6			7	83	90
7			14	92	91
8			6	90	70
9			12	77	86
10			9	77	80
11			5	68	38
12[d]			5	44	53
13[d]			5	49	49

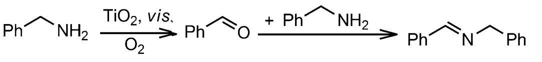
[a] Reaction conditions: amine (0.2 mmol), CH_3CN (5 mL), air (1 atm), TiO_2 (anatase, 50 mg; Alfa Aesar, 130 m^2g^{-1}), Xe lamp (300 W, cutoff wavelengths below 420 nm). [b] Determined by GC analysis using bromobenzene as the internal standard. [c] Selectivity = yield/conversion. [d] About 3% of acetophenones were found in the product.

(44%, 49%) were achieved at a moderate conversion rate (53%, 49%).

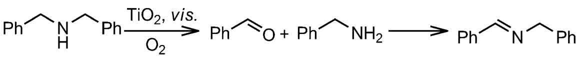
The reaction profile for the oxidation of benzylamine is shown in Figure 2. From the experimental results, we can conclude that the reaction obeys zero-order kinetics. At relatively low conversion rates, the benzylamine could be transformed into the corresponding imine with excellent selectivity. However, with a prolonged reaction time and a higher conversion of benzylamine, a slight decrease in the selectivity for the imine would occur and small amounts of benzaldehyde appeared in the products. This result is because the increased consumption of benzylamine in the solution could not ensure the full condensation of the nascent aldehyde and the amine, which is in agreement with the proposed mechanism in Scheme 1, in which an aldehyde intermediate is present in the formation of the imine.

The formation of imine involves a selective oxyxgenation step and a further condensation step. The overall process can be simply summarized in Equation (1). Along this line, the formation of imines from secondary benzylic amines should proceed according to Equation (2). As the newly generated benzylamine could be further transformed following Equation (1). Thus, the oxygenation products, the corresponding aldehydes, should be observed for the oxidation of these substrates, acting as a crucial mechanistic evidence for Scheme 1. The results of the oxidation of a series of secondary benzylic amines are summarized in Table 3 (entries 1–5). Significant amounts of benzaldehyde or its derivatives were observed for all these substrates (Table 3, entries 1–14), which is a clear indication that an oxygenation process still dominates the formation of imines under visible-light irradiation.

For asymmetric dibenzylic amines (Table 3, entries 6 and 7), in addition to the two corresponding benzaldehydes, four imines products were observed for each substrate; this result



(2)



(3)

further confirms the sole involvement of an oxygenation step leading to the final product distribution rather than the involvement of an an oxidative dehydrogenation process. When *N*-benzyl-1-phenylethylamine was chosen as the substrate (Table 3, entry 8), benzaldehyde, acetophenone, and imine products were all observed; these products were pre-

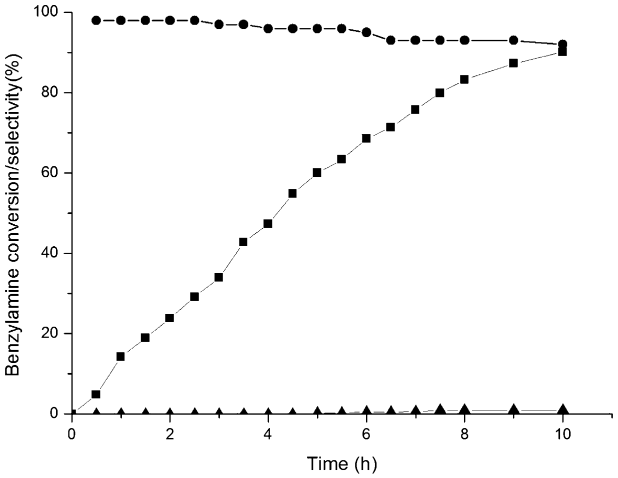
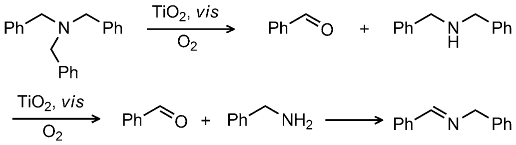


Figure 2. Reaction profiles for the oxidation of benzylamine on a TiO_2 surface under visible-light irradiation. Conversion of benzylamine (■), selectivity for the imine (●), selectivity for benzaldehyde (▲). Reaction conditions: benzylamine (0.2 mmol), CH_3CN (5 mL), TiO_2 (anatase, 50 mg; Alfa Aesar, 130 m^2g^{-1}), Xe lamp (300 W, cutoff below 420 nm), air (1 atm).

sumably formed by the activation of the benzylic carbon–hydrogen atoms on both sides of the nitrogen atom. The oxidation of *N*-benzyl-4-methoxyaniline (Table 3, entry 9), in which only one benzylic carbon atom is present, afforded benzaldehyde and 4-methoxyaniline products; the difficulty of the condensation reaction between benzaldehyde and 4-methoxyaniline prevented the formation of the imine.

As an aliphatic amine could be further partially degraded under these conditions, benzaldehyde was present in excess. Because the corresponding aliphatic radicals lack the required stability under the photocatalytic conditions, C_α–H activation of the aliphatic arm only affords benzylamine, which can be further oxidized according to Equation (1) to produce the other imine. However, C_α–H activation is preferred at the benzyl group and this pathway affords the majority of the observed products, i.e. benzaldehyde and the imine (formed by condensation between benzaldehyde and either benzylamine or an aliphatic amine; Table 3, entries 10–12). For substrates without a C_α–H bond on the aliphatic arm (Table 3, entry 13), only the C_α–H bond on the benzyl arm can be activated to selectively generate benzaldehyde and one imine, which is formed from a coupling reaction between benzaldehyde and *tert*-butylamine. We used a cyclopropyl group as the intramolecular radical trap to verify the radical nature of this reaction (Table 3, entry 14); only benzaldehyde and *N*-benzylidenebenzylamine were detected as the final products and no cyclopropyl groups were found intact, thereby suggesting that the reaction proceeds through a radical intermediate. The oxidation of 1,2,3,4-tetrahydroquinoline afforded 3,4-dihydro-quinoline with a relative high selectivity (68 %; Table 3, entry 15).

According to Scheme 1, when tribenzylamine was chosen as the substrate, the product profiles should follow Equation (3). Benzaldehyde, dibenzylamine, and *N*-benzylidenebenzylamine were the main products with selectivities of 39 %, 24 %, and 27 %, respectively. The formation of the corresponding imine from tribenzylamine also proceeded through an oxygenation step followed by condensation which agrees well with the mechanism in Scheme 1.



(4)

As the product formation is governed by the proposed mechanism in Scheme 1, it is reasonable to obtain excellent selectivities and relatively low conversion rate (Table 1). It is for the same reason that we observed very good selectivity and very high conversation rates for the reactions shown in Table 2 (except for a few cases that might be caused by instability of the imine product, such as Table 2, entry 11), even though they are slight lower than the results in Table 1. Furthermore, the relationship of conversion versus selectivity allows us to understand the results for the substrates in Table 3 according to the mechanism in Scheme 1. As a result, we can only achieve moderate conversion rates and moderate selectivities for the imines products in Table 3.

Conclusion

We have discovered that a series of benzylic amines adsorbed onto the surface of TiO_2 could extend light absorption into the visible range. This feature can be used for the aerobic oxidation of amines into their corresponding imines under visible-light irradiation in inert solvents. In addition to the synthetic significance, this finding gave us a unique opportunity to understand the concerted interactions of dioxygen with photogenerated free-radicals and electrons on the conduction band of TiO_2, excluding the influence of holes in the valence band of TiO_2 under UV irradiation, which give us a clearer picture of the activation of dioxygen and its influence on the selectivity of the products in TiO_2 photocatalysis. The formation of imines proceeds via an oxygenation pathway rather than an oxidative-dehydrogenation process; in this oxygenation pathway, oxygen-transfer from dioxygen to the substrates is the main oxidation step under visible-light irradiation. These findings will deepen our understanding of the role of dioxygen in TiO_2 photocatalysis and will offer a general mechanistic framework for aerobic-oxidation reactions involving semiconductor photocatalysis. Furthermore, new heteroatom-containing substrates might be oxofunctionalized in dioxygen or in air on TiO_2 surfaces under visible-light irradiation.

Table 3. Aerobic oxidation of secondary and tertiary benzylic amines on a TiO_2 surface under visible-light irradiation.[a]

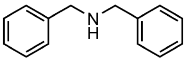
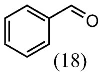
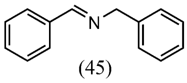
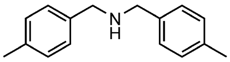
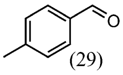
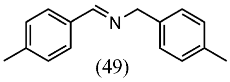
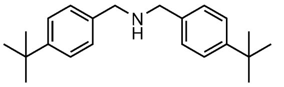
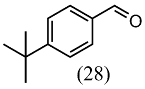
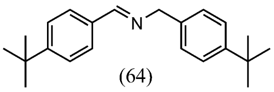
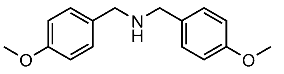
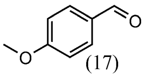
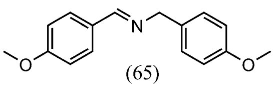
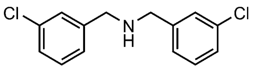
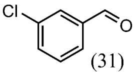
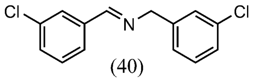
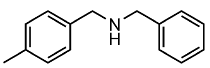
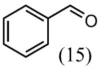
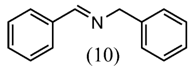
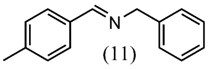
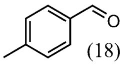
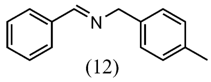
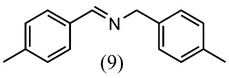
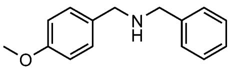
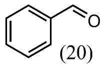
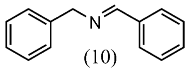
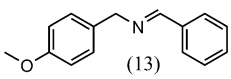
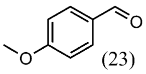
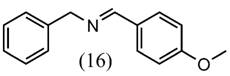
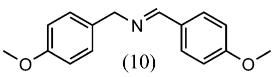
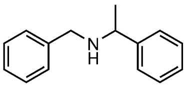
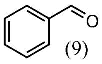
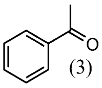
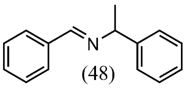
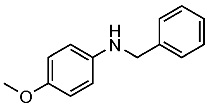
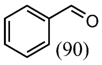
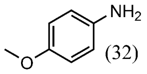
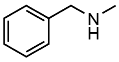
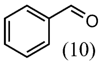
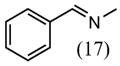
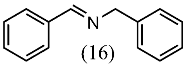
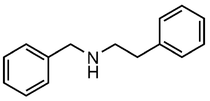
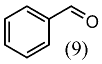
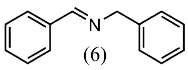
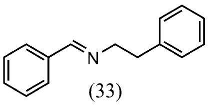
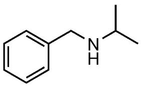
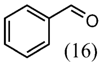
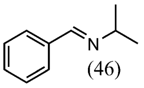
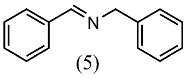
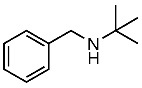
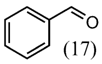
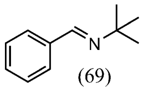
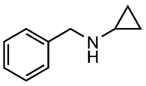
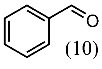
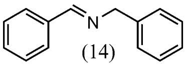
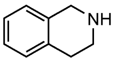
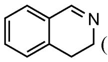
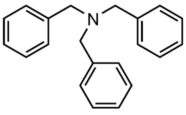
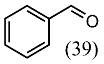
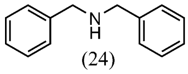
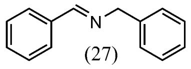
Entry	Substrate	*t* [h]	Conv. [mol %][b]	Products [mol %][c]
1		8	81	 (18)  (45)
2		8	66	 (29)  (49)
3		8	44	 (28)  (64)
4		8	75	 (17)  (65)
5		8	70	 (31)  (40)
6		5	79	 (15)  (10)  (11)  (18)  (12)  (9)
7		5	74	 (20)  (10)  (13)  (23)  (16)  (10)
8		8	62	 (9)  (3)  (48)
9		5	18	 (90)  (32)
10		4	67	 (10)  (17)  (16)
11		4	36	 (9)  (6)  (33)
12		4	63	 (16)  (46)  (5)
13		4	69	 (17)  (69)
14		4	100	 (10)  (14)
15		5	100	 (68)

Table 3. (Continued)

Entry	Substrate	t [h]	Conv. [mol %][b]	Products [mol %][c]
16		8	50	 (39)  (24)  (27)

[a] Reaction conditions: amine (0.1 mmol), CH_3CN (5 mL), air (1 atm), TiO_2 (anatase, 50 mg; Alfa Aesar, 130 m^2g^{-1}), Xe lamp (300 W, cutoff wavelengths below 420 nm). [b] Determined by GC analysis using bromobenzene as the internal standard. [c] Determined by GC analysis using bromobenzene as the internal standard; values in parentheses show the selectivity for the desired product (yield/conversion).

Experimental Section

Materials and instruments: All reagents and solvents were obtained commercially and used without further purification. GC measurements were made on a Hitachi GC 3900 equipped with a standard FID detector and a DM-5 amine capillary column (5% polysilarylene, 95% polydimethylsiloxane, 30 m, 0.5 mm × 0.25 μm, Dikma) using highly pure N_2 as the carrier gas.

Standard analytical conditions: Injector temperature: 250 °C, FID detector temperature: 300 °C, column temperature program: 80 °C (hold 3 min) to 280 °C (hold 5 min) at 20 °C min^{-1}. GC-MS analysis (Thermo-Finingan Trace 2000/Trace DSQ) was carried out with a DB-5MS capillary column (30 m, Dikma) and highly pure He as the carrier gas.

Typical procedure for the oxidation of amines: The photocatalytic reactions were carried out under irradiation by a Xe lamp (300 W, PLS-SXE 300, Beijing Trusttech Co.), equipped with a cutoff filter to filter out light below 420 nm and a broad band filter to cutoff light above 750 nm, with magnetic stirring in a 10 mL Pyrex glass bottle. The bottle was sealed with a rubber stopper wrapped in aluminum foil and opened to air through a syringe needle. A typical reaction system consisted of the substrate (0.2 mmol) and TiO_2 (anatase, 50 mg) in CH_3CN (5 mL). The temperature of the reaction medium was around 40 °C. After filtering through a Millipore filter to remove the TiO_2 powder, the reaction mixture was analyzed by GC using bromobenzene as the internal standard. The products were confirmed by comparison of retention times with authentic samples and by GC-MS analysis.

Acknowledgements

Financial support from the National Basic Research Program of China (973 project No. 2010CB933503), the National Natural Science Foundation of China (NSFC, Nos. 20920102034, 21077110 and 20877076), and the Chinese Academy of Sciences (CAS) are gratefully acknowledged.

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Received: July 21, 2011
Revised: September 23, 2011