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Photocatalytic conversion of nitroaromatic compounds in the presence of TiO_2

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ABSTRACT

The combination of a solid photocatalyst (TiO_2) and a co-catalyst (*p*-toluenesulfonic acid) has been successfully applied for the light-induced conversion of five different derivatives of nitrobenzene (*o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT), 5-nitro-*m*-xylene (DMNB), and *p*-nitrophenol (*p*-NPh)) in O_2-free ethanolic suspensions yielding substituted quinolines and tetrahydroquinolines. GC–MS analysis of the irradiated mixtures showed the formation of substituted quinolines as the main products when DMNB, *m*-NT, and *p*-NPh were employed as substrates, while ethoxy-tetrahydroquinolines were obtained when *o*- and *p*-NT were used. DMNB has been chosen as model substrate for a more detailed study focusing on the influence of the concentration of the photocatalyst, the co-catalyst, and the nitroaromatic compound on the yield of the products. Depending on the compounds that have been detected by GC–MS the reaction mechanism is discussed.

1. Introduction

The development of highly selective and environmentally benign chemical conversion processes to synthesize chemical specialties is an important subject in chemistry. Unfortunately, the required selectivity often comes at the expense of specially designed metal catalysts or reagents which have adverse environmental effects. One encouraging approach is to use nontoxic catalysts such as TiO_2 in the presence of sunlight, which is a safe and sustainable energy source, as a driving force for the reaction [1].

Since the discovery of the photocatalytic properties of TiO_2, this heterogeneous photocatalyst has been mainly employed to degrade organic and inorganic pollutants in water or air [2]. Different from that, the application of this catalyst for organic synthesis is a very attractive and significant target of research, which, however, is often neglected. The fact that some chemical reactions only occur in photocatalytic systems is more significant for this application. A few examples, such as the photocatalytic cyclization of α,ω-diamines [3], the synthesis of unsaturated N-phenyl-α-amino esters [4] and unsaturated α-cyano-homoallylamines [5], the light-induced carbon–carbon bond formation [6], and the diastereoselective radical tandem addition-cyclization reactions of aromatic tertiary amines [7] have been reported.

Quinoline and its derivatives have been the subject of much research due to their importance in various applications and their widespread biochemical significance. A large variety of quinoline derivatives have been used as antimalarial, anti-inflammatory agents, antiasthmatic, antibacterial, antihypertensive and tyrokinase PDGF-RTK inhibiting agents [8]. Furthermore, poly-substituted quinolines have been found to undergo hierarchical self-assembly into a variety of nano- and mesostructures with enhanced electronic and photonic properties [9–11]. In view of these properties, great efforts have been made to develop new and efficient synthetic routes to quinoline derivatives in both synthetic organic and medicinal chemistry. The structural core of quinoline has generally been synthesized by various thermal reactions usually referred as Skraup, Doebner-von Miller, Friedländer, Pfitzinger, Conrad-Limpach, Combes synthesis [12]. These classical syntheses are well known and still frequently used for the preparation of pharmaceutical agents, ligands and functional materials bearing a quinoline backbone.

Jia et al. have used *p*-toluene sulfonic acid (*p*-TsOH) to catalyze the synthesis of quinolines through Friedländer condensation of a 2-aminoarylketone or a 2-aminoarylaldehyde with carbonyl compounds [13]. But because of the relative instability of *o*-aminoaldehyde, which can readily undergo self-condensation, Brian et al. developed a one-pot analogue of the Friedländer synthesis [14], in which the intermediate *o*-aminobenzaldehyde was not isolated, but rather immediately converted in situ to a quinoline using catalytic amounts of $CrCl_2$ in the presence of Mn or Zn dust and TMSCl (trimethylsilyl chloride).

Faraway from thermal synthetic routes to quinolines, heterogeneous photocatalysts open a new way for the synthesis of heterocyclic compounds [15]. Photoexcitation of TiO_2 particles at wavelengths exceeding the band gap energy promotes electrons into the conduction band (CB) leaving positive holes in the valence band (VB). If electrons and holes reach the surface of the semiconductor

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before they recombine, these charge carriers can induce redox processes of organic substrates present at or near the surface of the semiconductor. A variety of organic functional transformations mediated by irradiation of semiconductors have been reported [16]. It is well established that a primary alcohol can be easily photocatalytically oxidized on the semiconductor surface to its corresponding aldehyde [17]. Mahdavi et al. have reported that under UV irradiation of a solution of a nitro compound in a primary alcohol in the presence of suspended TiO_2 particles an amino compound as the reduced product as well as an aldehyde as the oxidized product are formed in high yields [18]. For multistep synthesis an illuminated semiconductor does offer a unique feature. An intermediate generated at one reactive site (oxidative or reductive) can be the substrate at another reactive site. The integrated use of both reactive sites can complete a sophisticated multistep synthesis in "one pot". The objective of this work is to investigate the feasibility of using these photocatalytic redox reactions in the presence of TiO_2 and *p*-TsOH as a co-catalyst for the synthesis of quinolines via the reduction of nitroaromatic compounds and the oxidation of ethanol.

2. Experimental

2.1. Small scale

In a typical experimental run 25 mg TiO_2 (Sachtleben Hombikat UV100) was suspended in 10 cm^3 of an ethanolic solution (Roth) containing 100 μmol of the nitroaromatic compound (Aldrich) and the required amount of *p*-TsOH (Aldrich) and irradiated by a 500-W mercury medium-pressure lamp Heraeus TQ 718 Z4 (UV(A) intensity = 15 mW/cm^2) after purging with Ar for 30 min. The reaction was performed in a glass snap-cap bottle (23 mm in diameter and 75 mm in length) under continuous stirring. Samples were taken during the reaction and analyzed by GC/MS after removing the semiconductor particles through filtration (0.45 μm) from the irradiated mixture. For GC/MS analysis, a Shimadzu gas chromatograph and mass spectrometer (GC–MS-QP 5000) equipped with a 30 m Stabilwax-DA (d = 0.32 mm) capillary column was used. Operating temperature programmed: injection temperature 280 °C, oven temperature 70 °C (hold 2 min) from 70 °C to 240 °C at the rate of 12 °C/min, 240 °C (hold 15 min) in split mode, injection volume (3.0 μl) with helium as a carrier gas.

2.2. Large scale

The reaction was performed in a photoreactor consisting of a cylindrical Pyrex glass batch reactor (volume = 1 l) equipped with a 500-W mercury medium-pressure immersed lamp Heraeus TQ 718 Z4. The reaction temperature was maintained at 298 K by recirculating distilled water between a Pyrex glass jacket surrounding the reactor and a thermostat. TiO_2 (1 g) was suspended in 350 ml ethanol and the reactor was purged with Ar for 30 min. DMNB (20 mmol) and *p*-TsOH (1 mmol) were solved in 50 ml ethanol. Aliquots (1 ml) of this solution were added to the TiO_2 suspension every 10 min. After about 10 h the catalyst was removed by filtration and the solvent was evaporated by rotavapor. The formed trimethylquinoline was isolated from the dark orange oily residual by column chromatography using silica gel as the stationary phase and a n-hexane:ethyl acetate 8:2 (v/v) mixture as the eluent. The structure of the product was determined on the basis of the ^1H NMR and ^{13}C NMR spectra recorded in $CDCl_3$ by a 200 MHz spectrometer.

2,5,7-Trimethylquinoline was synthesized according to a reported method [19] and purified by column chromatography.

3. Results

The conversion of *o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT), 5-nitro-*m*-xylene (DMNB), and *p*-nitrophenol (*p*-NPh) in Ar-purged ethanolic suspensions containing TiO_2 as the photocatalyst and *p*-TsOH as a co-catalyst under irradiation with UV light was investigated. The respective anilines as well as the corresponding quinolines and tetrahydroquinolines were identified as products of the reactions of these compounds by GC–MS. GC–MS chromatograms recorded at different reaction times of the photocatalytic conversion of DMNB in ethanol are presented in Fig. 1 as a typical example. 2,5,7-Trimethylquinoline (TMQ) and 3,5-dimethylaniline (DMA) were identified as products of the reaction of DMNB. The products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library and/or with those of reference compounds that have been synthesized by independent methods. Substituted quinolines were also obtained as the main products when *m*-NT and *p*-NPh were employed as substrates, while ethoxy-tetrahydroquinolines were obtained when *o*-NT and

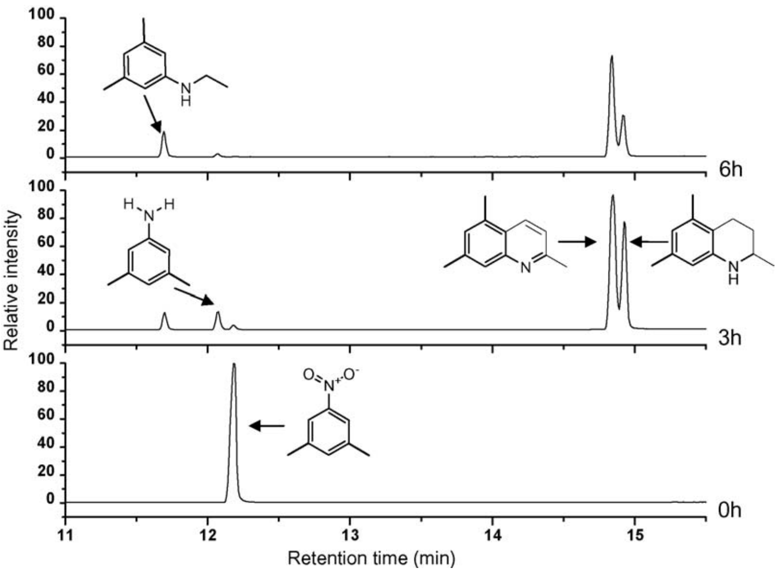


Fig. 1. GC/MS chromatograms at different reaction times for the photocatalytic conversion of DMNB (*reaction conditions*: 100 μmol DMNB, 25 mg TiO_2, and 5 mol% *p*-TsOH in 10 ml EtOH, 15 mW $UV(A)/cm^2$, ambient temperature, under Ar).

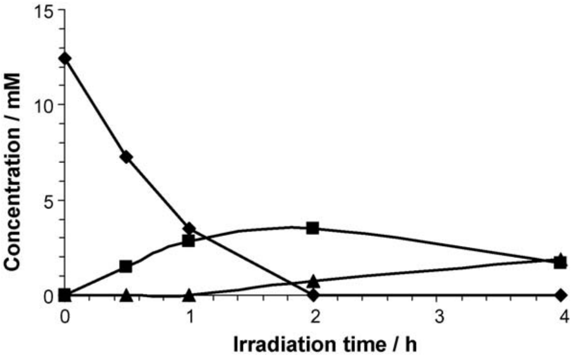


Fig. 2. Time course of the photocatalytic conversion of DMNB; (◆) DMNB, (■) DMA, (▲) TMQ. (*reaction conditions*: 100 μmol DMNB and 25 mg TiO_2 in 10 ml EtOH, 15 mW UV(A)/cm^2, ambient temperature, under Ar).

p-NT were used (data not shown), clearly indicating that the abundance of the different products depends on the substituents of the nitro aromatic compound employed as starting material.

After stirring the mixtures in the dark for several hours as well as after irradiation of the ethanolic solutions of the nitro aromatic compounds in the absence of TiO_2 no cyclization products were detected (data not shown) clearly indicating that TiO_2 and UV light are essential for the reaction. To elucidate this type of reaction in more detail DMNB was chosen as the model substrate to study the influence of the concentration of *p*-TsOH, of the TiO_2 concentration, and the initial concentration of the nitro aromatic compound on the formation of the cyclization product TMQ.

Fig. 2 shows the time course of the DMNB consumption and the product formation under UV irradiation of a reaction mixture containing TiO_2, DMNB, and ethanol, but no *p*-TsOH. After 2 h of irradiation DMNB is converted by 100%. At this time the colour of the suspension changed from white to blue due to the trapping of photogenerated electrons by Ti(IV) to form Ti(III), indicating the complete conversion of the electron acceptor DMNB. During this time (2 h) the amount of the intermediate DMA reaches the maximum then it is further converted to produce TMQ. However, the yield of TMQ is small.

To increase the yield of TMQ, varying amounts (5, 10, 20, and 40 mol%) of *p*-TsOH were added to the reaction mixture. The yields of TMQ at different reaction times are given in Fig. 3. From this figure it can be seen that the yield of TMQ was significantly increased from 6% in the absence of *p*-TsOH to 50% (46.7% isolated yield in large scale experiment) when only a small amount of *p*-TsOH (5 mol%) was added. However, upon the addition of 40 mol% of *p*-TsOH the yield is only increased from 50% to 60%. This result prompted us to use an amount of 5 mol% *p*-TsOH as a co-catalyst in further studies.

UV irradiation of ethanolic solutions of DMNB in the presence of 5 mol% *p*-TsOH and varying amounts of TiO_2 (1.25, 2.5, and 5 g/l) shows a significant effect of the TiO_2 concentration on the required time for total photocatalytic conversion of DMNB (Fig. 4). Increasing the TiO_2 content from 1.25 g/l to 2.5 g/l increases the reaction rate of DMNB significantly, whereas the increase in the TiO_2 concentration to values higher than 2.5 g/l results in decreasing rates of DMNB conversion and decreasing TMQ yields. Thus at an amount of TiO_2 exceeding 2.5 g/l all of the incident photons are absorbed by the suspension. Based on this data, the catalyst amount used in the further runs was 2.5 g/l.

In another set of experimental runs the influence of the initial concentration of DMNB (10–80 mmol/l) on the conversion of DMNB, the yield of TMQ, and the selectivity for TMQ formation was investigated; the respective experimental results are given in Table 1. It becomes obvious that the reaction time required for complete DMNB conversion increases with increasing initial DMNB concentration. When 10 mmol/l DMNB was used 100% conversion was achieved within 2 h of UV irradiation, while 4 h were required for complete conversion in the case of 20 mmol/l and more than 6 h for higher concentrations. Long irradiation times negatively affect both the yield and the selectivity of TMQ production (cf. Table 1).

4. Discussion

Scheme 1 provides a tentative overview of plausible reaction mechanisms leading to the cyclization products identified by GC–MS. The first steps in the reaction which are necessary for all following reactions are the photocatalytic reduction of the nitro group of the nitroaromatic compound and the photocatalytic oxidation of the alcohol. The nitro aromatic compound is directly reduced to aniline by photogenerated conduction band electrons on the semiconductor's surface; simultaneously the alcohol is dehydrogenated to the corresponding aldehyde consuming the photogenerated valance band holes of the illuminated TiO_2. It is well known that the photocatalytic formation of an aldehyde from an alcohol occurs via formation of an α-hydroxylradical as the one-electron oxidation product of the alcohol [20].

The light-induced six-electron reduction of a nitro compound in the presence of TiO_2 occurs via a sequence of electron transfer, protonation, and dehydration reactions (cf. Scheme 2). The complete reduction of one nitro group to an amino group requires six electrons and six protons. In an irradiated deaerated TiO_2 slurry containing an alcohol and a nitro organic compound, α-hydroxyalkyl radicals which are known to be powerful reducing agents with reduction potentials lower than −1.0 V vs the NHE [21] may react with the photocatalyst surface (current doubling), or they

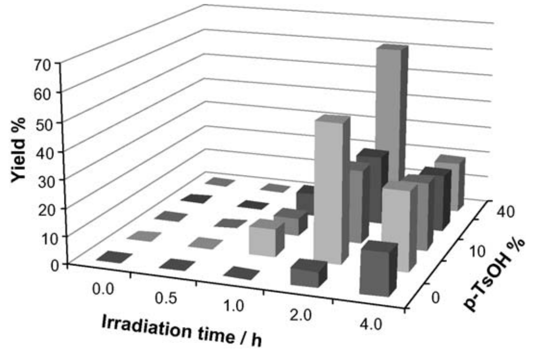


Fig. 3. Time course of the yield of TMQ at different *p*-TsOH concentrations (*reaction conditions*: 100 μmol DMNB, 25 mg TiO_2, and required amounts of *p*-TsOH in 10 ml EtOH, 15 mW UV(A)/cm^2, ambient temperature, under Ar).

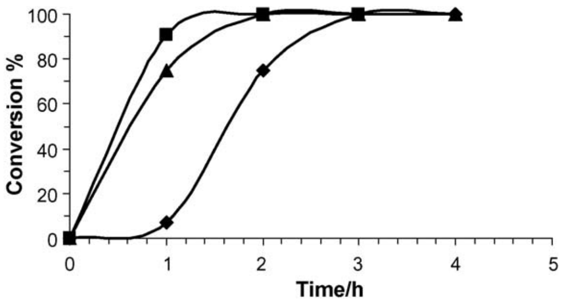


Fig. 4. Effect of the TiO_2 concentration on the photocatalytic conversion of DMNB; (◆) 1.25 g/l, (■) 2.5 g/l, (▲) 5 g/l (*reaction conditions*: 100 μmol DMNB, 5 mol% *p*-TsOH, and required amount of TiO_2 in 10 ml EtOH, 15 mW UV(A)/cm^2, ambient temperature, under Ar).

Table 1
Effect of the concentration of DMNB on its photocatalytic conversion, the yield of TMQ, and the TMQ selectivity (*reaction conditions*: 5 mol% *p*-TsOH, 25 mg TiO_2 and required amount DMNB in 10 ml EtOH, 15 mW UV(A)/cm^2, ambient temperature, under Ar).

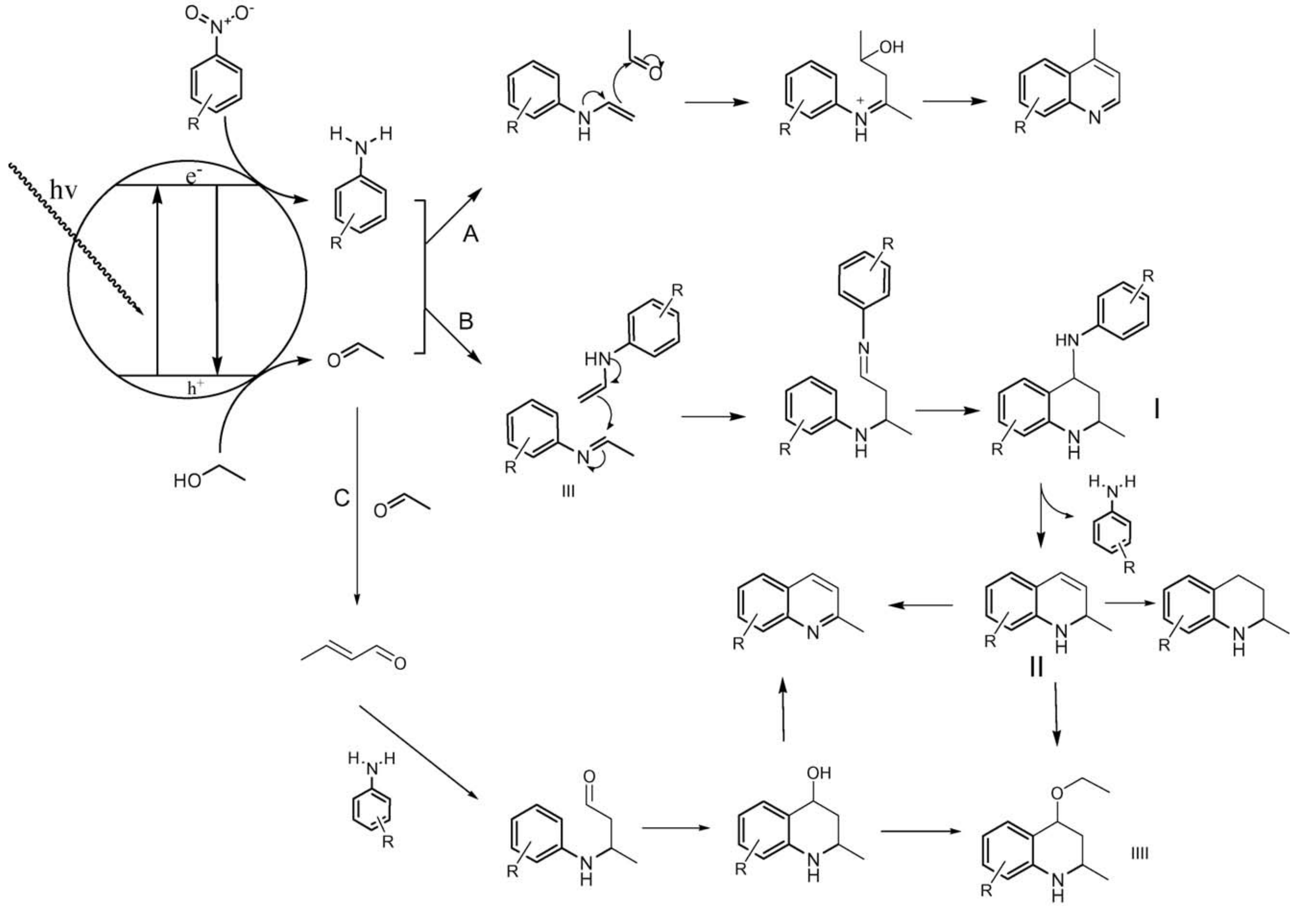
Run	Reaction time (h)	DMNB initial concentration (mM)	Conversion (%)	TMQ	
				Yield (%)	Selectivity (%)
1	2	10	100	50	50
2	2	20	89	15	16
3	2	40	13	6	43
4	2	80	>5	–	–
5	4	10	100	29	29
6	4	20	100	33	33
7	4	40	52	12	22
8	4	80	12	4	30
9	6	20	100	31	31
10	6	40	82	18	21
11	6	80	20	6	31

may react with the nitro organic compound directly. Ferry and Glaze who have investigated the mechanism of the photocatalytic reduction of aromatic and aliphatic nitro compounds at the surface of TiO_2 in the absence of oxygen and in the presence of a sacrificial electron donor (methanol or isopropanol) have shown that conduction band electrons (free or trapped as Ti(III)) are the principal species driving the reactions of nitro compounds to amino compounds. Secondary radicals generated from alcohol oxidation by valence band holes played no role in the formation of the amino compounds [22].

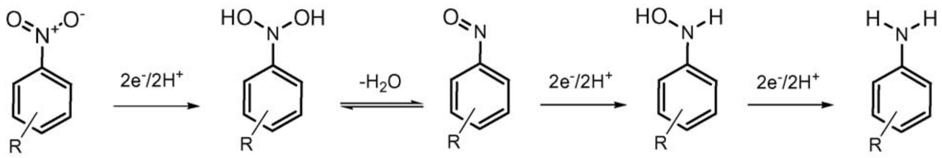
Pathways A and B (Scheme 1) suggest the formation of an imine (Schiff base) via the reaction between the aniline and acetaldehyde formed photocatalytically at the TiO_2 surface, whereas pathway C requires the intermediate formation of croton aldehyde, the product of an aldol condensation of two acetaldehyde units, which reacts with the aniline.

Because of the lower calculated heat of formation for TMQ compared with that for 4,5,7-trimethylquinoline (93.6 and 262.3 kJ/mol, respectively [23]), the low reaction temperature favors the formation of TMQ (pathway B or C in Scheme 1). Note that croton aldehyde was not detected by GC–MS under the experimental conditions of this work.

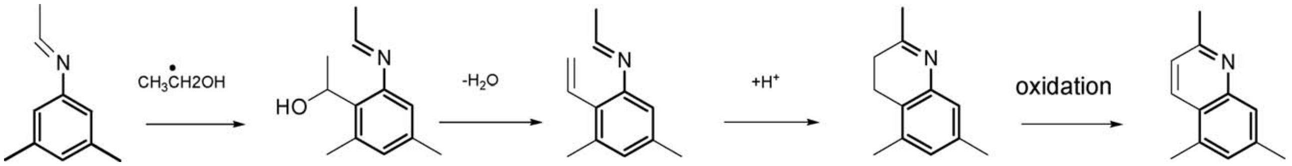
On the other hand, N-ethyl-3,5-dimethylbenzenamine (EB) has been detected by GC/MS as a byproduct. The formation of EB is the result of hydrogen transfer from ethanol to the C=N moiety of the Schiff base. Although the detected amount of EB was small



Scheme 1. Schematic overview over the possible reaction pathways.



Scheme 2. Schematic illustration for the reduction of a nitroaromatic compound to an aminoaromatic compound.



Scheme 3. Schematic illustration for the *ortho*-alkylation pathway.

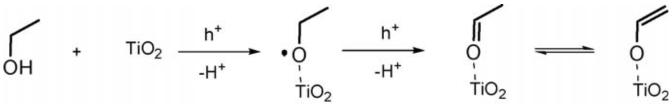
compared with the amount of the cyclization product its formation suggests that the Schiff base is a reaction intermediate.

Condensation of amines with aldehydes is usually conducted by refluxing the reactants in a solvent forming an azeotrope with water, thus removing the water formed during the reaction and shifting the equilibrium toward the imine. The ability of TiO_2 to adsorb the produced water may help to separate it from the reaction mixture.

Another evidence for the reaction pathway B is the formation of tetrahydroquinoline which was also detected by GC/MS. 1,2,3,4-tetrahydro-2,5,7-trimethyl-N-(3,5-dimethylphenyl) quinoline-4-amine (I) can be formed via cycloaddition of the imine (III) to its enamine tautomer. Subsequent elimination of an aniline molecule yields the dihydroquinoline (II) as intermediate. This intermediate can suffer depending on the position of the substituent (*o*-, *m*-, and *p*-) or its type (methyl or hydroxyl) in the starting substrate, either disproportionation (in case of DMNB, *m*-NT, *p*-NPh) to produce substituted quinolines and tetrahydroquinolines or reaction with the ethanol (in case of *o*- and *p*-NT) to produce ethoxy-tetrahydroquinoline (IIII) as the main product. These results are in a good agreement with results published by Forrest et al. who demonstrated the viability of a mechanism for the thermal synthesis of 2-methylquinoline from aniline and acetaldehyde in the liquid phase that does not involve the formation of an α,β-unsaturated aldehyde [24].

p-TsOH added to the reaction mixtures may play several roles. First it can catalyse the reaction of the aniline with the acetaldehyde, both formed photocatalytically at the TiO_2 surface, which requires acidic conditions[13]. We noticed that the production and consumption of the aniline compound occur during the first 2 h in the presence of *p*-TsOH, whereas, in the absence of *p*-TsOH the aniline is still detected even after 4 h of irradiation (see Fig. 2); secondly, it can improve the restriction of the product readsorption charging both the TiO_2 surface and the cyclization products positively. On the other hand, conversion of 1,2,3,4-tetrahydro-2,5,7-trimethyl-N-(3,5-dimethylphenyl)quinolin-4-amine (I) to the final products via the dihydroquinoline compound (II) is catalyzed by acid [25]. This reasoning can explain the increase in the yield of TMQ by adding *p*-TsOH. However, an excess of acid will protonate both nitrogens in compound (I) resulting in an inhibition of the reaction [25].

Two other possible mechanisms can also be envisaged. As illustrated in Scheme 3 the α-hydroxylradical, which is produced during the photocatalytic oxidation of ethanol, can attack the aromatic ring of the formed aniline (or its derived imine) in the *ortho* position to form the hydroxyethylated derivatives, followed by dehydrations, H-shifts, and intramolecular acid-catalyzed reaction to form the quinoline compound. Although Brosius et al. suggested a similar mechanism for the vapor-phase synthesis of 2-methyl- and 4-methylquinoline over BEA* zeolites [26], to the best of our knowledge. This mechanism has not yet been confirmed.



Scheme 4. The possible surface adsorption and reaction mechanism of the photocatalytic oxidation of ethanol.

The second mechanism suggests the formation of titanium enolate on the surface of TiO_2. Chen et al. reported that the oxidation of ethanol occurs favorably as a surface reaction. End group adsorption (molecular stand-up adsorption on the surface; cf. Scheme 4) of the alcohol on the photocatalytic surface may occur leading to enolate formation [27]. This enolate can condensate with the Schiff base to produce hydroquinoline derivatives that are photocatalytically oxidized yielding the corresponding quinoline.

The data for the reaction of DMNB obtained by GC–MS analysis supports the proposed mechanism according to pathway B in Scheme 1. It becomes obvious from the chromatograms given in Fig. 1 that the nitro compound (retention time 12.40 min) is consumed and trimethylquinoline (retention time 14.85 min) is formed. The appearance of the peaks at retention time 12.09 min and 11.70 min reveals the formation of DMA and EB indicating the reduction of the nitro group to an amino group which condensates with the acetaldehyde. The peak at retention time 14.95 min ($m/z = 175$) is a good indication of the disproportionation mechanism.

5. Conclusion

Substituted quinolines and other heterocycles can be prepared from ethanolic solutions of substituted nitrobenzenes by a TiO_2 nanoparticles mediated photocatalytic process. The ratio of the cyclization products (quinolines, tetrahydroquinolines, and ethoxy-tetrahydroquinolines) depends on the position (*o*-, *m*-, and *p*-) or the type (methyl or hydroxyl) of the substituent of the nitrobenzene used as starting material. In the photocatalytic reaction of an ethanolic solution of DMNB the yield of TMQ as the cyclization product was found to be influenced by the concentration of TiO_2, and the presence of *p*-TsOH as a co-catalyst. Based on the compounds detected by GC/MS a reaction mechanism is proposed comprising the formation of methylanilines and acetaldehyde by a photocatalytic reaction step and their subsequent reaction to quinolines and tetrahydroquinolines via a Schiff base as an intermediate product.

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References

[1] H. Tada, T. Ishida, A. Takao, S. Ito, S. Mukhopadhyay, T. Akita, Koji Tanaka, H. Kobayashi, ChemPhysChem 6 (2005) 1537.
[2] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[3] S.-I. Nishimoto, B. Ohtani, T. Yoshikawa, T. Kagiya, J. Am. Chem. Soc. 105 (1983) 7180.
[4] M. Hopfner, H. Weiß, D. Meissner, F.W. Heinemann, H. Kisch, Photochem. Photobiol. Sci. 1 (2002) 696.
[5] H.C. Pehlivanugullari, E. Sumer, H. Kisch, Res. Chem. Intermed. 33 (2007) 297.
[6] L. Cermenati, C. Richterb, A. Albinia, Chem. Commun. (1998) 805.
[7] S. Marinkovic, N. Hoffmann, Eur. J. Org. Chem. (2004) 3102.
[8] M.P. Maguire, K.R. Sheets, K. McVety, A.P. Spada, A. Zilberstein, J. Med. Chem. 37 (1994) 2129.
[9] X. Zhang, A.S. Shetty, S.A. Jenekhe, Macromolecules 32 (1999) 7422.
[10] X. Zhang, S.A. Jenekhe, Macromolecules 33 (2000) 2069.
[11] S.A. Jenekhe, L. Lu, M.M. Alam, Macromolecules 34 (2001) 7315.
[12] V.V. Kouznetsov, L.Y.V. Méndez, M.M. Gómez, Curr. Org. Chem. 9 (2005) 141.
[13] C.S. Jia, Z. Zhang, S.J. Tu, G.W. Wang, Org. Biomol. Chem. 4 (2006) 104.
[14] B.R. McNaughton, B.L. Miller, Org. Lett. 5 (2003) 4257.
[15] K.H. Park, H.S. Joo, K. Ahn, K. Jun, Tetrahedron Lett. 36 (1995) 5943.
[16] M. Qamar, M. Muneer, D. Bahnemann, Res. Chem. Intermed. 31 (2005) 807.
[17] F.H. Hussein, G. Pattenden, R. Rudham, J. Russell, J. Tetrahedron Lett. 25 (1984) 3363.
[18] F. Mahdavi, T.C. Bruton, Y. Li, J. Org. Chem. 58 (1993) 744.
[19] C.M. Leir, J. Org. Chem. 42 (1977) 911.
[20] C.Y. Wang, R. Pagel, D.W. Bahnemann, J.K. Dohrmann, J. Phys. Chem. B 108 (2004) 14082.
[21] H.A. Schwarz, R.W. Dodson, J. Phys. Chem. 93 (1989) 409.
[22] J. Ferry, W.H. Glaze, Langmuir 14 (1998) 3551.
[23] M. Campanati, P. Savini, A. Tagliani, A. Vaccari, Catal. Lett. 47 (1997) 247.
[24] T.P. Forrest, G.A. Dauphinee, W.F. Miller, Can. J. Chem. 47 (1969) 2121.
[25] T.P. Forrest, G.A. Dauphinee, W.F. Miller, Can. J. Chem. 52 (1974) 884.
[26] R. Brosius, D. Gammon, F. van Laar, E. van Steen, B. Sels, P. Jacobs, J. Catal. 239 (2006) 362.
[27] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Water Res. 33 (1999) 669.