Res Chem Intermed (2010) 36:937–945
DOI 10.1007/s11164-010-0206-6

Photocatalytic reaction of aryl amines/alcohols on TiO_2 nanoparticles

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Received: 24 December 2009 / Accepted: 17 September 2010 / Published online: 28 November 2010

Abstract In this article, the photocatalytic reaction of aniline and 4-amino N, N dimethyl aniline with methanol, ethanol and isopropanol on anatase TiO_2 nanoparticles under UV (365 nm wavelength) irradiation was examined. The concentration of unreacted aryl amines and products was measured by gas chromatography picks integration, and then the products were identified by mass spectroscopy analysis. By making a comparison within the rates of photocatalysis of each aryl amine in different alcohols under various irradiation times, it was revealed that, in all cases, the sequence of photocatalysis rate was methanol $>$ ethanol $>$ isopropanol. In reactions where the concentrations of aryl amine were lower than 10 mmol/L, imines were the main products and alkylation of amines was not observed. In the higher concentration of aryl amines, oxidation and dimerization occurred.

Keywords Photocatalytic reaction · Aryl amine · TiO_2 nanoparticle · GC–MS analysis

Introduction

Heterogeneous photocatalysis has been extensively investigated as a possible way for removal of pollutants [1–3], organic synthesis [4–6] and bactericidal activity [7]. Nanosized titania powder is a widely used semiconductor photocatalyst owing to its non-toxic nature, chemical stability, availability, low cost and capability of easy preparation in nano-particulate form with high surface area [8].

The initial step in TiO_2-mediated photocatalytic degradation is proposed to involve the generation of an (e^-/p^+) pair, leading mainly to the formation of

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hydroxyl radicals (·OH) as well as super oxide radical anions ($O_2^{\cdot -}$) and hydroperoxy radicals (·OOH). These radicals are oxidizing species in the photocatalytic oxidation processes [9, 10]. Among the above-mentioned radicals of which TiO_2 are produced by photocatalysis, hydroxyl radicals are the most powerful oxidizing species that can attack organic contaminants present at or near the surface of TiO_2 particles [11]. In heterogeneous photocatalysis studies involved with semiconductor powders, thermodynamic and kinetic aspects, surface area and photocatalyst particle size are important factors for the identification of the reaction product [12].

In recent years, photocatalysis reaction of TiO_2 on aryl amines has attracted many researchers due to its considerable application in organic dye industries [12–16]. The mechanism of TiO_2-photocatalyzed degradation of aniline derivatives in acidic and alkaline mediums has been studied by Canle et al. [12]. They have reported that photocatalytic degradation of aryl amines in acidic medium was inhibited due to electrostatic repulsion between the positively charged surface and protonated amines, while in an alkaline medium, the main photoproduct of degradation of aniline is nitrobenzene. As an example in an alkaline medium, degradation of aniline has been investigated using an alkaline aqueous TiO_2 suspension containing carbonate ions [17]. The presence of carbonate in TiO_2 suspension increases the number of active adsorption sites on TiO_2 particle surfaces. The major products in this reaction were identified to be azobenzene, p-benzoquinone, nitrobenzene, and NH_3. Although aniline at ppm level is mineralized by illuminated TiO_2, in higher concentrations it is oxidized to azobenzene [13]. N-alkylation of amines by photocatalytic reaction in a microreaction system using Pt-free TiO_2 and Pt-loaded TiO_2 has been investigated [18]. It was reported that the N-alkylation did not occur by the irradiation of Pt-free TiO_2 in conventional batch reactor. To cut a long story short, there has been a lot of interest in the photocatalytic reaction of aryl amines on TiO_2, but the results reported in the literature are partly controversial.

In the current work, we have investigated the photocatalytic reaction of two aryl amines (aniline and 4-amino N, N dimethyl aniline) using TiO_2 nonopowder suspension in alcohols (methanol, ethanol and isopropanol); the products of photoreaction were followed by GC-Mass analysis.

Experimental

Synthesis of photocatalyst

Nanopowder anatase TiO_2 samples were synthesized by the precipitation method and dehydrated with the azeotropic distillation technique, as we have reported in previous work [8]. The sizes of nanopowders obtained after calcinations were 15–25 nm and the surface area measured by BET method was 75–80 m^2/g.

Photocatalytic activity

The aryl amines (aniline and 4-amino N, N dimethy aniline) were dissolved separately in methanol, ethanol and isopropanol with 1–10 mmol/L concentrations.

A sample of 20 mg synthesized TiO_2 nanopowder was added to each Pyrex volumetric balloon containing 10 ml of the aryl amine solution. The contents of the balloons were sonicated in an ultrasound bath for 10 min. The aryl amines solution, in the presence and in the absence of TiO_2, were irradiated for 1–40 h by five UV lamps ($\lambda = 360$ nm) with 40 W power, in an irradiation box.

Analysis

The reactions products were analyzed by gas chromatograph–mass selective detector (GC–MS) from Agilent Technologies, GC—6890 N and MS—5973 N model, with the column HP-5, length 30 m, i.d. 0.25 mm and film thickness 0.25 µm. The employed GC condition was: initial temperature 100 °C, hold 3 min with the ramp rate 8 °C/min and final temperature 250 °C. The concentration of unreacted aryl amine and products was obtained from integration of chromatogram picks.

Results and discussions

Aryl amines are widely used as raw materials in organic dye industries and are known as highly toxic chemicals. Two aryl amines which were chosen in this experiment are aniline (An) and 4-amino N, N dimethyl aniline (ADA).

First, 10 ml of ADA solutions in alcohol (methanol, ethanol, isopropanol) with 5 mmol/L concentration and 20 mg TiO_2 nanopowder were sonicated for 10 min, and then irradiated under 40 W UVA. The rate of decreasing of ADA concentration is shown in Fig. 1. As shown in this figure, the rate of photocatalytic degradation of ADA in methanol is higher than ethanol and isopropanol, respectively. After 40 h irradiation in the presence of TiO_2 nanopowder, ADA completely disappeared in methanol and ethanol. However, the concentration of ADA in isopropanol reduced

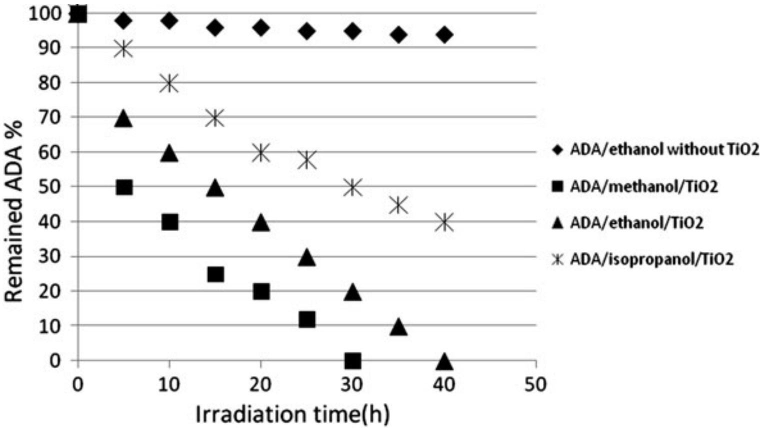


Fig. 1 Variations of ADA concentrations (%) in alcohol as a function of the irradiation time. The samples were 10 ml ADA in alcohol with 5 mmol/L concentration and 20 mg TiO_2

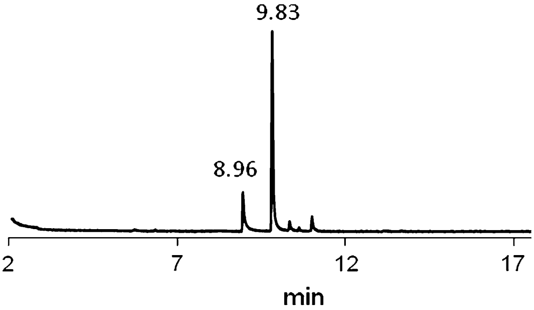


Fig. 2 Chromatogram of photocatalytic reaction product of ADA and methanol after 20 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 9.83 is the main product

slowly and,after 24 h,only 20% of initial concentration was decomposed. To compare the results, a blank experiment was carried out on ADA/ethanol solution in the absence of TiO_2 particles. ADA did not effectively degrade under similar conditions (see Fig. 1).

The chromatogram of photocatalytic reaction products of ADA and methanol is displayed in Fig. 2. The pick in the 8.96-min retention time (RT) corresponds to ADA and the pick in the RT = 9.83 min corresponds to the major product. The mass spectra of major product are shown in Fig. 3. All the picks in mass spectra are matched with 4 (methylene amino) phenyl dimethyl amine (1). The photocatalytic reaction products of ADA/ethanol solution after 30 h irradiation are shown in Fig. 4. This chromatogram shows two major products in RT = 11.01 and RT = 11.68. The mass spectrum of the first product is shown in Fig. 5. This spectrum confirms the formation of 4 (ethylene amino) phenyl dimethyl amine (2), while dialkenylation may be occurring in ethanol (RT = 11.68). So, from the obtained results, we can propose the reaction process as shown in Scheme 1 for imines formation.

However, the rate of reaction in isopropanol was lower than the other two alcohols. The chromatogram of this reaction products, after 24 h irradiation, is shown in Fig. 6, and mass spectrum of the major product (RT = 11.71 min) is shown in Fig. 7. The addition of isopropenyl on amine is confirmed by characteristic picks in m/e 176, 161, 145, 120, 105 and 77.

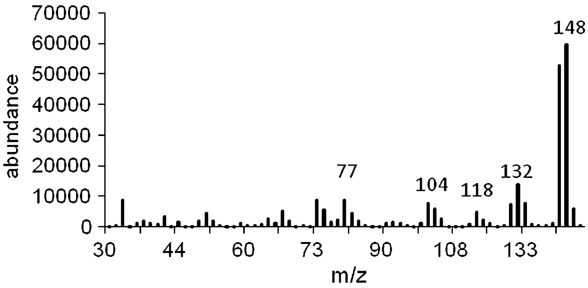


Fig. 3 Mass spectra of the main product of ADA and methanol with TiO_2 (from GC–MS spectroscopy, RT = 9.83). The mass spectra completely matched with 4(methylene amino) phenyl dimethyl amine

Fig. 4 Chromatogram of photocatalytic reaction product of ADA and ethanol after 30 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 11.01 and RT = 11.68 are the main products

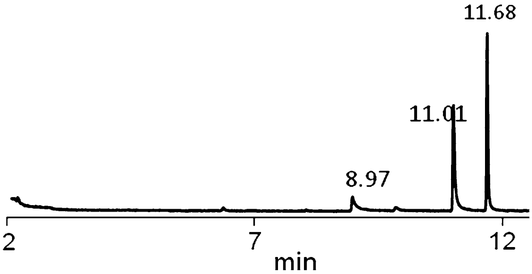
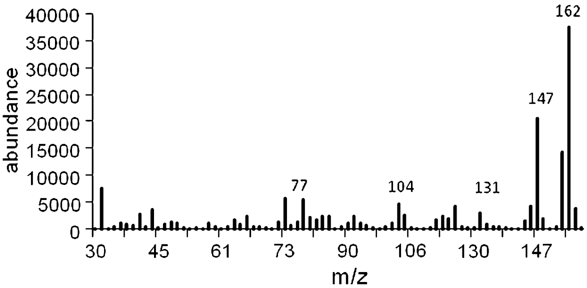
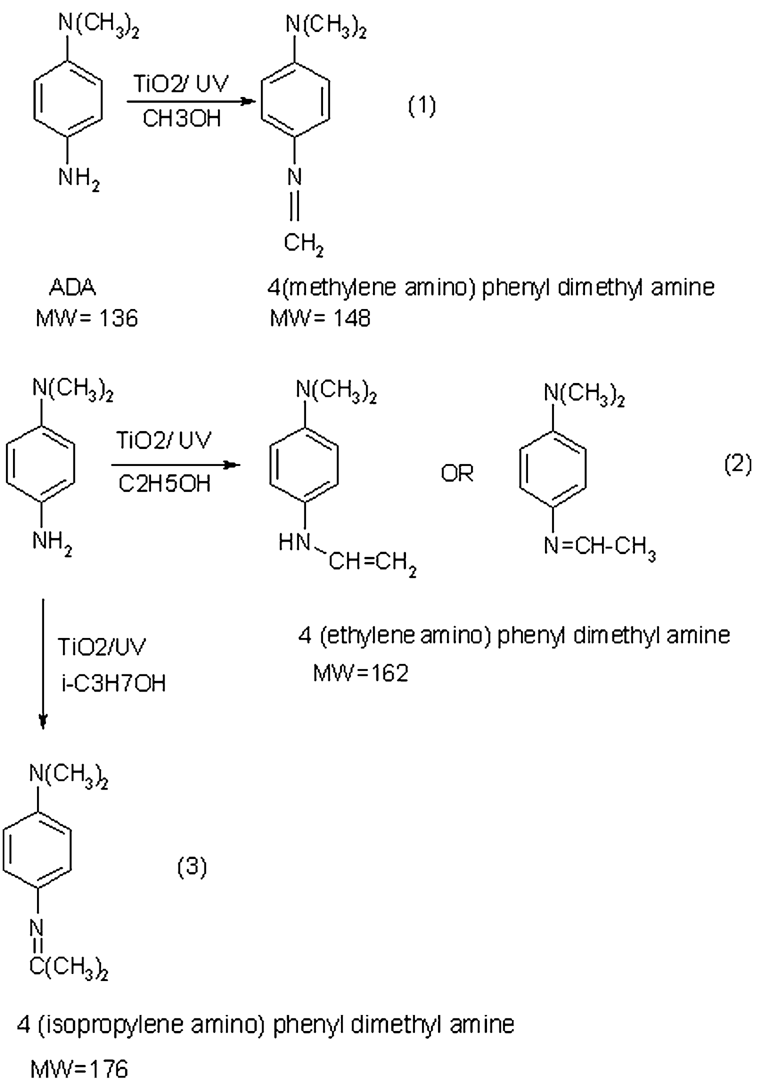


Fig. 5 Mass spectra of the main product of ADA and ethanol with TiO_2 (from GC–MS spectroscopy, RT = 11.01). The mass spectra completely matched with 4 (ethylene amino) phenyl dimethyl amine



After a long period of UVA irradiation (about 70 h) in the presence of TiO_2, ADA was completely decomposed in methanol and ethanol. But, during the same length of time, ADA in isopropanol was converted to various compounds. Although in the photodegradation process, especially in higher concentration ($\geq$50 mmol), dimerization of aryl amine with the violet color may be occurring, in the lower concentration ($\leq$5 mmol/L) ADA did not dimerize.

The rate of photocatalytic reaction of aniline in alcohol was higher than ADA. Figure 8 shows the decreasing rate of aniline in the 10 ml aniline/alcohol solutions with 1 mmol/L concentration of aniline in the presence and absence of TiO_2. As shown in this figure, aniline remained unchanged in the absence of TiO_2 after 5 h irradiation and, similar to the ADA, photocatalytic reaction of aniline–methanol and aniline–ethanol is more effective than isopropanol. The chromatogram of photocatalytic reaction of aniline in methanol after 3 h is shown in Fig. 9. During the 3-h reaction time, more than 82.5% of aniline was converted to other compounds. In this chromatogram, the pick in the RT = 2.97 corresponds to the aniline and the pick in the RT = 2.68 corresponds to the product. The mass spectra of this product match completely with N-methylene amino phenyl (the mass spectra are displayed in Fig. 10). During this time, the number of products in ethanol is greater and a small amount of 2-methyl quinoline is considered additional to N-ethylene amino phenyl. In the higher concentration of more than 50 mmol/L, various products, e.g., azo benzene, azoxy benzene and 4-phenyl azo phenol, were formed. Scheme 2 shows the reaction process of photocatalytic reaction of aniline in alcohols.



Scheme 1 Alkenylation of ADA in alcohol in the presence of TiO_2 under UV (365 nm) irradiation

To investigate the reason for the lower reaction rate of aryl amine in isopropanol, the pure isopropanol with TiO_2 nanopowder was irradiated under UVA lamps. As a result, various compounds were produced. The products of reaction were acetone, isopropyl ortho formate and acetaldehyde diisopropyl acetate as identified by GC–MS analysis. A condensation reaction between amines and ketones or aldehydes (from photocatalytic reaction of alcohols) may have produced imine or enamine compounds. The photocatalytic reaction of alcohol with longer chain is more complex and leads to the formation of various products. This can be attributed to the formation of numerous radical species which finally react together perfectly.

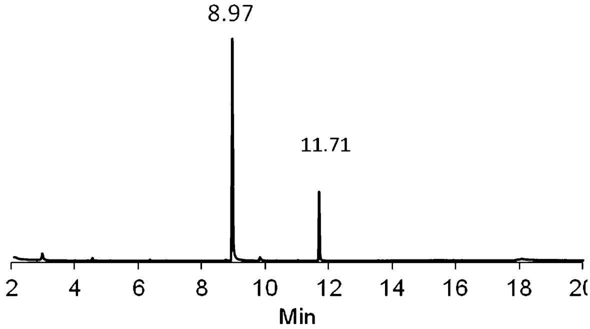


Fig. 6 Chromatogram of photocatalytical reaction product of ADA and isopropanol after 24 h irradiation. The pick at RT = 8.96 min corresponds to ADA and RT = 11.71 is the main product

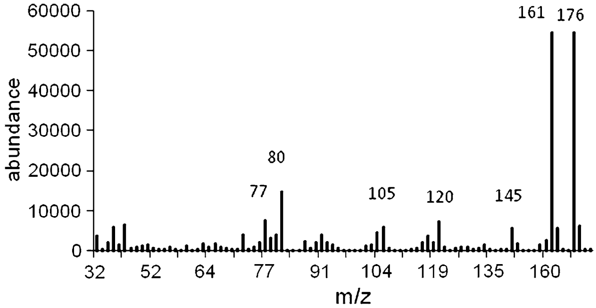


Fig. 7 Mass spectra of the main product of ADA and isopropanol with TiO_2 (from GC–MS spectroscopy, RT = 11.71). The mass spectra completely matched with 4(isopropylene amino) phenyl dimethyl amine

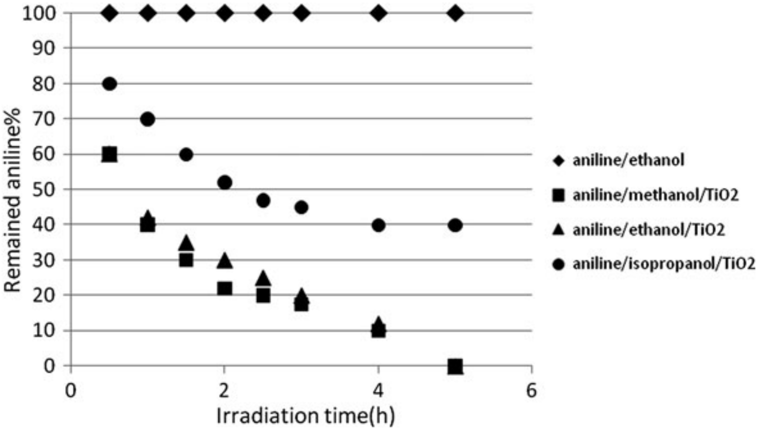


Fig. 8 Variations of aniline concentrations (%) in alcohol as a function of the irradiation time. The samples were 10 ml aniline in alcohol with 1 mmol/L concentration and 20 mg TiO_2

Conclusions

Samples containing aryl amine/alcohol and TiO_2 nanopowder suspensions were irradiated with 40-W UVA lamps. The GC–Mass analysis showed the imine formation in the concentration of lower than 10 mmol/L. The imines can be

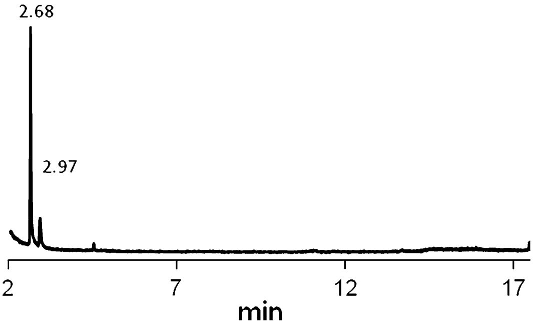


Fig. 9 Chromatogram of photocatalytic reaction product of aniline and methanol after 3 h irradiation. The pick at RT = 2.97 min corresponds to aniline and RT = 2.68 is the main product

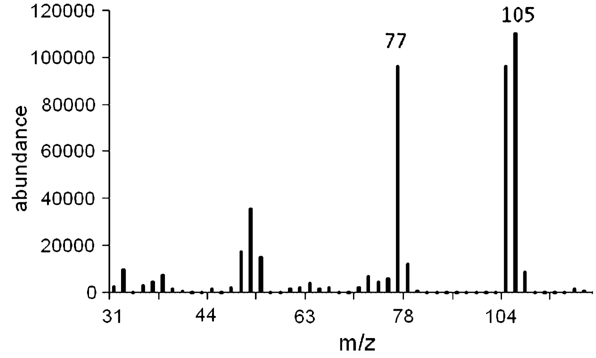
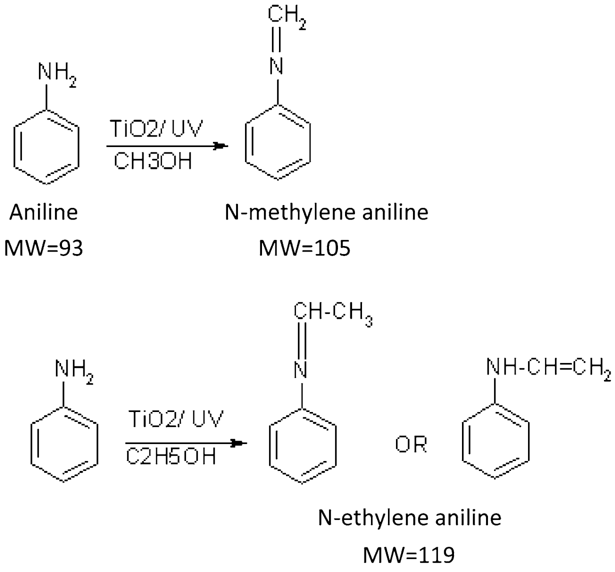


Fig. 10 Mass spectra of the main product of aniline and methanol with TiO_2 (from GC–MS spectroscopy, RT = 2.68). The mass spectra completely matched with N-methylene aniline



Scheme 2 Alkenylation of aniline in alcohol in the presence of TiO_2 under UV (365 nm) irradiation

isomerized to the enamines form. The sequence of photocatalytic reaction rate was methanol > ethanol > isopropanol. Investigation into these reaction mechanisms showed that active radicals of alcohols form in the presence of TiO_2 under UVA irradiation and that these radicals initiate the reactions. The reason for the difference in reaction rate corresponds to the stability of formed radicals from alcohol. Also, the variety of radicals from isoprpanol is more than two other alcohols, so the radicals react together perfectly. In the higher concentration (more than 10 mmol), oxidation of aryl amine occurs and some products, e.g., azobenzene, azoxy benzene, 4-phenyl azo phenol and some of their derivatives, are formed. In the results of these reactions, the alkylation of aryl amines is not observed in any of the reaction studies.

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