Synthesis of imines from nitrobenzene and TiO₂ particles suspended in alcohols via semiconductor photocatalysis type B

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ABSTRACT

UV irradiation on a non-aqueous suspension of titanium dioxide with nitrobenzene and different alcohols in deaerated conditions produces imines and aniline as main products. The conversion of nitrobenzene and the corresponding selectivity of imines or aniline depend on the type of alcohol used. A low conversion (3–12%) and selectivity close to 100% to imines were obtained with methyl, ethyl, or propyl alcohol. Otherwise, using i-propanol only aniline was detected with a conversion of 13%. Finally, a mixture of aniline and imines was formed employing n-butyl, n-amyl, and i-amyl alcohols with the higher conversion ($\sim$50%).

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1. Introduction

Imine, also known as azomethine, is formed by the reversible condensation between amine and carbonyl groups. This reaction was discovered by the German chemist Hugo Schiff in 1864 and since then imines are also called as Schiff's bases.[1] An imine is a chemical compound containing a carbon–nitrogen double bond with a general structure $R_1R_2C=NR_3$ used as key intermediate for the synthesis of nitrogen heterocycles.[2] Imine synthesis is catalyzed with acids and since it implies a condensation reaction, it is necessary to eliminate the water as formed.[3] Therefore, the exploration of new methods that have a minimal environment impact and low cost is necessary.

Organic synthesis through semiconductor photocatalysis has become an important research area in photochemistry for the last two decades.[4,5] Many reactions, such as oxidation, reduction, and isomerization of organics, C–H bond activation, C–C and C–N bond forming have been studied using different photocatalysts.[4–8] The most studied photocatalytic reaction has been the oxidation of organic compounds in water because common semiconductors have band edges that lie positive of the oxidation potentials of most organic functional groups. By contrast, photocatalytic reductions are less frequently found, because the reducing power of a conduction band electron is significantly lower than the oxidizing power of a valence band electron.[8] It is well known that the reduction of nitroarenes can occur easily as a result of their direct light absorption and then, they are among the most studied photochemical systems.[9,10] In addition, the photocatalytic reduction of nitroarenes has been also reported using different semiconductors and operation conditions.[4,9–18] This reaction can be carried out in the presence of a large excess of a sacrificial electron donor (SED).[9–11] To scavenge valence band holes is the main function of the sacrificial electron donors in order to limit the charge recombination degree and then liberating more reductive species.[12] Many solvents, such as alcohols, organic acids, and their mixtures have been reported as useful SED in order to improve the global photoredox cycle.[9–18] However, it is not still clear what the influence is of the type of alcohol added on the selectivity during the photocatalytic reduction of nitrocompounds. In a previous work,[13] we have studied the photocatalytic reduction of nitrobenzene using ethanol as SED finding a low selectivity to aniline and the formation of by-products such as indoles and quinolines. Note that the nature of the obtained products should be explained in terms of the specific mechanistic scheme of semiconductor photocatalysis classified into two categories accordingly.[19–22] Semiconductor photocatalysis type A means that at least one reduced and one oxidized compounds are obtained and reactions such as dealkylation, cyclization, and hydroalkylation can also occur.[7] On the contrary, photocatalysis type B after forming the photoredox products can react under dark conditions by using the catalytic properties of the semiconductor yielding new products.

In the present work, we report a new approach of photocatalytic reduction of nitrobenzene and its derivatives by using a non-aqueous suspension of titanium dioxide to observe the effect of several aliphatic alcohols (C_1–C_5) on the conversion and selectivity.

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2. Results and discussion

Irradiation with UV-light ($\lambda \approx 365$ nm) of an alcoholic suspension of titanium dioxide containing nitrobenzene (outgassed to discard the presence of oxygen) yields imines or amines. In a blank experiment, irradiation of an alcoholic solution of nitrobenzene alone led to no reaction product, indicating that TiO_2 was essential for the reaction. On the other hand, without irradiation under UV-light, no reaction product was detected either.

Irradiation for 24 h in the presence of alcoholic solvents gave the corresponding imines, aniline, or a mixture of imine/aniline without further reduction of imines (Table 1). The structure of each product was confirmed by GC/MS (see Supplementary data). As can be seen in Table 1, the conversion and selectivity were strongly solvent dependent. For short chain primary alcohols, C_1–C_3, nitrobenzene conversion exhibited values below 12% and the corresponding selectivities were close to 100% toward imines.

Isopropyl alcohol is a special case for its photocatalytic oxidation. Acetone is the only possible product to obtain and no subsequent reaction can take place. Nitrobenzene conversion just reaches 13%, similar to those of short chain alcohols. Besides, it has to be highlighted that selectivity toward aniline achieved 100%. An explanation of this behavior can be done in terms of the steric effect of acetone and acetaldehyde, the former is much less suitable to undergo condensation with aniline to form an imine.[23]
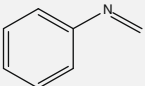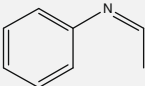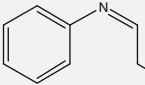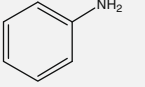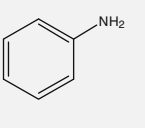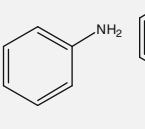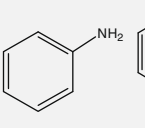
A different product distribution is observed for C_4–C_5 alcohols used as SEDs. An average nitrobenzene conversion value of 50% is achieved, that is, almost fivefold increase when compared to C_1–C_3 alcohols. Two products were found: aniline and imines. Aniline is the expected product f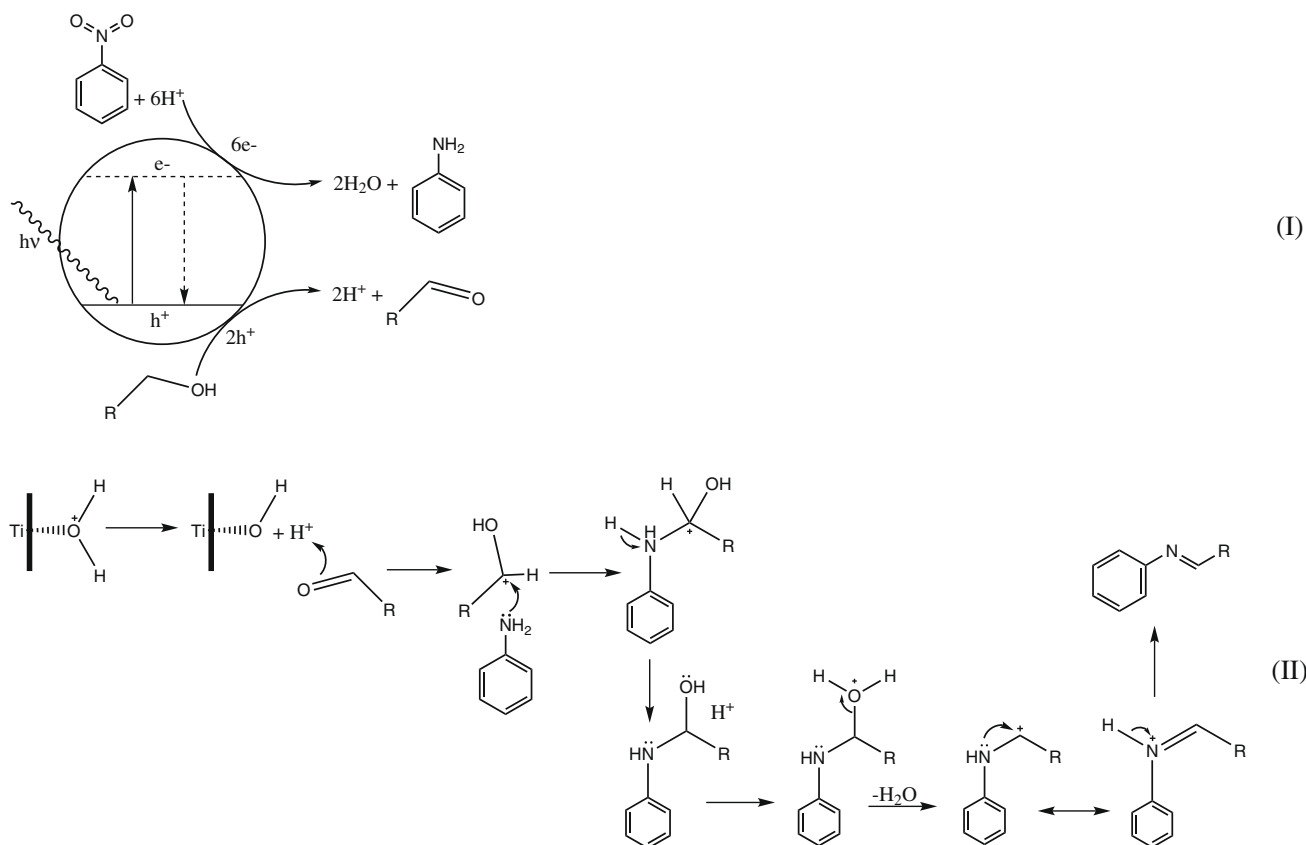or the photocatalytic reduction of nitrobenzene. However, imines, not expected, are also obtained. For all cases, selectivities for imines are higher than those for aniline. Although the conversion of nitrobenzene was higher than that for C_1–C_3 alcohols, the condensation reaction between aniline and the corresponding aldehyde was very slow which again must be explained by a steric effect using long chain alcohols.

These results indicated that the photocatalytic reduction of nitrobenzene was faster compared with the condensation reaction regardless of the type of alcohol used. However, for these experimental conditions, the condensation reaction is highly sensitive to the presence of oxygen in the reaction media. After irradiation, if the reactor is maintained open to the environment, the dissolved oxygen inside the reaction mixture favors the formation of indoles and quinolines.[16] On the contrary, if the reactor is maintained in nitrogen atmosphere a high selectivity to imines is obtained.

A reaction path for the production of imines or amines is proposed in two steps, as depicted in Figure 1. In the first step (I), the photoexcitation of TiO_2 occurs at wavelength corresponding to its band gap value, promoting electrons (e^-) in the conduction band and leaving positive holes (h^+). The photoreduction of nitrobenzene takes place only in the presence of a SED participating in the photoinduced process and sustaining oxidation and producing the electrons and protons required for the reduction of nitrobenzene.[9,10,17,18] In the second step (II), the process is carried out at dark conditions, the condensation between aldehyde and aniline forms an imine. In fact, the condensation reaction to form imines is catalyzed in acidic conditions that are provided by the TiO_2 surface. The acid sites could be titanol groups, Ti···OH, generated during the oxidation of alcohols.[24] It has been reported as a potential reaction, which includes the further reduction of imine into hydroxylamine depending on the thermodynamic equilibrium.[23] According

Table 1
Conversion of nitrobenzene and selectivity after 24 h of irradiation time as a function of the type of alcohol

Alcohol	Nitrobenzene conversion (%)	Reaction products	Selectivity (%)
Methanol	3		100
Ethanol	12		100
n-Propanol	9		100
i-Propanol	13		100
n-Butanol	54		15, 85
n-Pentanol	49		25, 75
i-Pentanol	52		42, 58

(I)

(II)

Figure 1. Proposed reaction mechanism for the photocatalytic formation of imines on TiO₂ suspension.

to our operation conditions, that reaction is favored to the formation of imines even though the presence of water shifts the equilibrium to imine reduction.

Further work is required in order to prove in more detail the role of the type of SED on yield to imines to have a one-pot synthesis at room temperature and atmospheric pressure.

3. Conclusion

Different kinds of imines have been prepared through a semiconductor photocatalysis type B in which the reduction product coming from nitrobenzene and the oxidation product of an alcohol are linked. It seemed that the rate-limiting step of the reaction network was the condensation between the aniline and aldehyde or ketone. When a C_1–C_3 alcohol is used as a solvent, a low conversion of nitrobenzene but almost 100% selectivity to the corresponding imine is obtained. If i-propanol is used only aniline is obtained. The long chain alcohols such as n-butyl, n-amyl, and i-amyl alcohols produce a mixture of aniline and imines. These results were explained in terms of a steric effect presented by each alcohol and with the presence of acid sites on the surface of TiO₂ which could be responsible for the conversion of aniline and aldehydes to imines.

4. Experimental

4.1. Materials

Titanium dioxide (TiO₂, Aldrich, 325 mesh, 98% anatase, 2% rutile) was used in all photocatalytic experiments in a concentration of 1 g/L. Methyl alcohol and ethyl alcohol were absolute grade (J.T. Baker); n-propyl alcohol was analytical grade (Merck); i-propyl, n-

butyl, n-amyl, and i-amyl alcohols were analytical grade (J.T. Baker). Nitrobenzene was high purity grade (>99%, Fluka). All reagents were used without further purification.

4.2. Methods

The alcoholic suspensions (5 mL) containing 126 mmol/L of nitrobenzene were prepared in a vial that was capped with butyl rubber septum, crimped with an aluminum seal, and then outgassed for 5 min in an ultrasonic bath. The suspensions were thoroughly purged with argon before irradiation. The irradiation was carried out with a black light lamp (15 W) for 24 h, under constant stirring and the vial was thermostated at 25 °C. After irradiation, the mixture was maintained closed and analyzed to identify the reaction products by means of a GC/MS system (Perkin–Elmer Autosystem XL-TurboMass) using a SPB-225 (Supelco) capillary column, 0.25 mm × 30 m. Gas chromatograph was operated with the following conditions: inlet temperature 200 °C, oven program: 130 °C (2 min), 230 °C (5 min), 17 °C/min. Blank experiments were carried out in order to discriminate the effect of TiO₂ or photochemical excitation.

Supplementary data

Supplementary data (mass spectrometry patterns for the reaction products) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.054.

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