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Photochemical and photocatalytic reduction of nitrobenzene in the presence of cyclohexene

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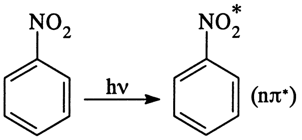
Abstract

Irradiation with light of wavelength higher than 350 nm of deaerated mixtures of nitrobenzene and cyclohexene leads to the reduction of the nitro-compound, with the formation of $C_6H_5N(O)=NC_6H_5$ (32%), $C_6H_5N=NC_6H_5$ (21%), $C_6H_5NH_2$ (15%), $C_6H_5N(H)C_6H_9$ (32%). The same stable reduction products are obtained when the photochemical experiments are carried out in the presence of powder dispersions of TiO_2 or WO_3 or CdS. On the other hand, the photocatalytic contribution of these semiconductors plays an important role in the relative product distribution, which is observed to depend on both competitive adsorption–desorption equilibria of the involved reagents and intermediates on the solid surface and the different reducing power of the photoexcited semiconductors. Cyclohexene participates in the photoinduced reduction of nitrobenzene, undergoing oxidation, and producing the required electrons and protons. Experimental evidence for the formation of radical species deriving from the oxidation of this alkene is obtained by ESR spin trapping investigation. We report here for the first time, the photoinduced allylic amination of cyclohexene with nitrobenzene to give the important building block of synthetic interest $C_6H_5N(H)C_6H_9$.

Keywords: Nitrobenzene photoreduction; Allylic amination; Photochemistry; Photocatalysis; Spin trapping; Semiconductors

1. Introduction

It has long been known that the reduction of nitroarenes can occur as a consequence of their direct light absorption [1–3]. In particular, evidence has been provided that this process proceeds upon irradiation in the near ultraviolet through the formation of an electrophilic nπ* triplet state as schematised by Eq. (1).



(1)

Nitroarenes have been also reduced with photoexcited particles of TiO_2 dispersed in aqueous media [4–10]. In fact, photoexcitation of semiconductors at wavelengths corresponding to the band gap value promotes electrons (e^-) in the conduction band leaving positive holes (h^+) in the valence band, as described by Eq. (2). If electrons and holes can reach the surface before recombination takes place, they can induce photocatalytic redox reactions. [11,12]

$$TiO_2 \xrightarrow{h\nu} TiO_2(h^+, e^-) \tag{2}$$

The photoinduced reduction of nitrobenzene should attract considerable interest in view of pursuing environmentally ‘benign’ or ‘green’ syntheses, since it consumes low-energy photons and occurs at atmospheric pressure and room temperature. A possible development to exploit the photoinduced reduction of nitroarenes for fine chemicals’ production consists in selecting appropriate cosubstrates whose role is not just that of transferring electron to the nitro-compound, but also that of generating reactive intermediates, which take part effectively in the formation of useful products. In this context, the use of alkenes as cosubstrates can provide an innovative way to induce interesting functionalisation reactions and, moreover, it represents a development of our research on the photocatalytic oxidation of hydrocarbons [13–15].

The present work has been carried out with the main purpose to investigate the mechanism of the photoinduced transformations of nitrobenzene in the absence of oxygen and in

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the presence of a simple unactivated alkene as cyclohexene. The identification of radical intermediates and stable products allows us to discuss both the direct photoreduction of nitrobenzene and the processes occurring in the presence of the following semiconducting photocatalysts: TiO_2, WO_3 and CdS. Moreover, we examine the possibility that the photoinduced processes may be of interest in view of synthetic applications.

2. Experimental details

2.1. Materials

Nitrobenzene and cyclohexene (Fluka) were distilled before use. TiO_2 was obtained from Degussa, while WO_3 and CdS from Strem Chemical. 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene) has been prepared following literature procedure [16] by Dr. Andrea Barbieri of the Department of Chemistry of Ferrara.

2.2. Irradiation procedure

Irradiation was carried out with a Oriel 6291 Xe/Hg lamp (2.5×10^2 mW cm^{-2}). Selection of excitation wavelengths was performed by using a glass filter which cuts off the light of wavelength lower than 350 nm. 3 ml of a mixture of cyclohexene and nitrobenzene (3:1 v/v) were irradiated for 3 h in a 1 cm spectrophotometric cell at 25±1°C. This amount of nitroaromatic compound is sufficient to absorb more than 90% of the incident light. When necessary, irradiation was performed in the presence also of powder semiconducting photocatalysts (4 g dm^{-3}). In these cases, the suspensions were continuously stirred during irradiation. Before irradiations, solutions or suspensions were deaerated by bubbling pure nitrogen. Blank experiments carried out in the absence of cyclohexene or photochemical excitation did not bring about any reduction of nitrobenzene.

2.3. Chromatographic conditions

All the analyses were performed with a Perkin Elmer Capillary Gas-Chromatograph using He as carrier gas. Column Restek Corporation Rtx-5 Amine (Crossbond 5% diphenyl–95% dimethyl polysiloxane; 30 m, 0.32 mm ID, 1.50 μm df). Recognition and identification of the products was obtained controlling the retention times with authentic amounts of the substances. $C_6H_5NH_2$, $C_6H_5N{=}NC_6H_5$ and $C_6H_5N(O){=}NC_6H_5$ were furnished by Aldrich. $C_6H_9{=}C_6H_9$ [17] and $C_6H_5N(H)C_6H_9$ [18] were, respectively, prepared by literature methods.

2.4. Spectroscopic experiments

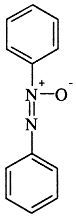
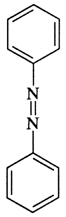
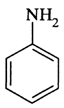
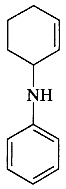
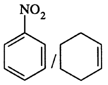
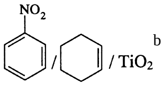
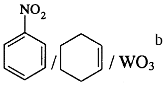
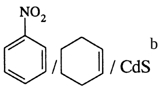
Previously deaerated mixtures of cyclohexene and nitrobenzene (3:1 v/v), were put in a quartz ESR flat cell. The employed semiconductors and/or spin trap were added when necessary. ESR spectra were collected with a Bruker 220 SE, X band, spectrometer, calibrated with α,α'-diphenylpicryl-hydrazil. Irradiation of the sample, directly in the ESR cavity was carried out with a medium pressure Hg lamp (λ>350 nm using a glass cut-off filter). No detectable paramagnetic signal was observed either in the dark or in the absence of cyclohexene.

UV–Vis diffuse reflectance spectra of semiconductor powder dispersions were obtained with a Lambda 6 spectrophotometer from Perkin Elmer, equipped with an integrating sphere.

3. Results

Photochemical experiments have been carried out irradiating, with light of wavelength higher than 350 nm, deaerated mixtures of cyclohexene and nitrobenzene (3:1 v/v), at room temperature and pressure. After 3 h irradiation, $(1.1\pm0.1)\times10^{-2}$ mol dm^{-3} of nitrobenzene were reduced to give the main products reported in Table 1. They account for about the 90% of the overall reduced nitrobenzene. Blank photochemical experiments carried out in the

Table 1
Photoinduced reduction of nitrobenzene in the presence of cyclohexene: main products and their relative distribution

Irradiated system[a]	Nitrobenzene reduction products			
	I	**II**	**III**	**IV**
				
	Product distribution[c] (%)			
	32	21	15	32
 [b]	11	47	19	23
 [b]	41	35	8	16
 [b]	28	11	46	15

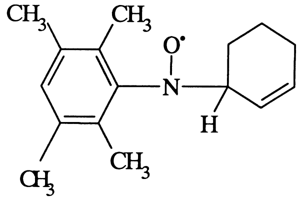
[a] 3 h irradiation (λ>350 nm) of deaerated mixtures cyclohexene/nitrobenzene 3:1 v/v at room temperature and pressure.

[b] 4 g dm^{-3} of powder photocatalyst were suspended in cyclohexene/nitrobenzene 3:1 v/v.

[c] The mass balance was found to be about 90% of reduced nitrobenzene ($(1.1\pm0.1)\times10^{-2}$ mol dm^{-3}).

absence of cyclohexene did not bring about any reduction of the nitro-compound. The results discussed here mainly focuses on the characterisation of nature and distribution of the nitrogen containing products. While the gas chromatographic analysis after irradiation revealed cyclohexene oxidation mainly to bicyclohexene, cyclohex-2-en-1-one and cyclohex-2-en-1-ol, a quantitative analysis of all the various possible oxidation products was not carried out at this stage of the work.

Direct evidence for the photoinduced formation of radical species deriving from cyclohexene oxidation is obtained for the first time by addition of nitrosodurene to the reaction mixture. This compound is known to react with radicals to give relatively stable paramagnetic nitroxides whose ESR spectra, in some instances, permit the identification of the trapped radicals. [19] After few seconds irradiation, we obtain the spectrum of Fig. 1. It consists of a triplet of doublets, with hyperfine splitting constants to the nitrogen A_N of 14 G and to the β-proton A_H of 8 G which can be attributed to the adduct (**A**) between nitrosodurene and a cyclohexenyl radical. When the ESR experiments were carried out in the absence of the spin trap, the superimposition of different unidentified paramagnetic species is obtained after about twenty minutes irradiation.



(A)

When the described photochemical experiments were carried out in the presence of powder dispersions of TiO_2 or WO_3 or CdS, the incident light (λ>350 nm) was absorbed by both the nitro-compound and the semiconductor. In fact, the absorption thresholds of TiO_2, WO_3, CdS and nitrobenzene were found to be 410, 470, 580 and 440 nm, respectively. We could not evaluate from a quantitative point of view the fraction of incident light that reached the semiconductor for two main reasons. First, because of the different absorption thresholds of the various chromophores; second, because the excitation light, before reaching the semiconductor particle, went through a thin layer of solution whose thickness was, however, indefinite due to non static conditions.

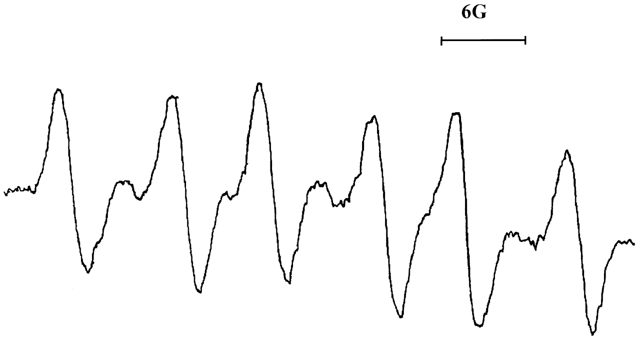
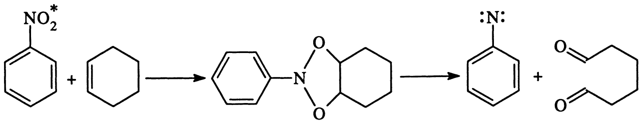


Fig. 1. ESR spectrum obtained during irradiation (λ>350 nm) of deaerated cyclohexene/nitrobenzene mixtures (3:1 v/v) in the presence of 2,3,5,6-tetramethylnitrosobenzene (5×10^{-3} mol dm^{-3}) as a spin trap.

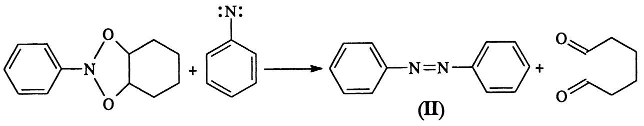
Photochemical excitation (λ>350 nm) of cyclohexene/nitrobenzene (3:1 v/v) deaerated mixtures containing the semiconductor led to the formation of the same amounts of paramagnetic intermediates and of the stable products already observed in the homogeneous phase. On the other hand, Table 1 shows that the photocatalytic contribution of the semiconductors strongly affected the relative product distribution. In particular, photocatalytic experiments carried out in the presence of TiO_2 gave (**II**) as main product with a selectivity higher than 40%, (**I**) with WO_3 and (**III**) with CdS.

4. Discussion

The photoinduced reactions of nitroarenes with cyclohexene were previously investigated by de Mayo and co-workers [3]. They demonstrated that irradiation induced cycloaddition of the nitro-group to the double bond giving the azobenzene (**II**) and an aldehyde product in a not completely characterised mixture of products through Eqs. (3) and (4).



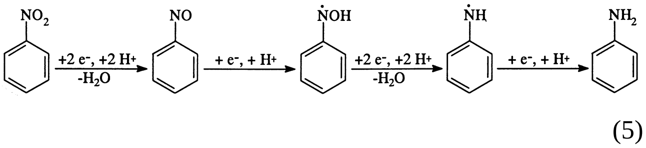
(3)



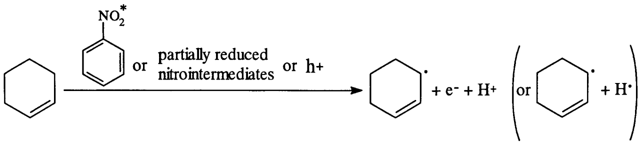
(**II**)

(4)

The data reported in Table 1 show that nitrobenzene can also undergo photoreduction until formation of aniline. Similar to the mechanism already proposed for the electrochemical reduction of nitro-compounds [20], this six-electron process can be described by Eq. (5), in which sequential electron transfers, protonations and dehydrations occur. Experimental evidence indicates that nitrobenzene photoreduction takes place only in the presence of cyclohexene, which is supposed to participate in the photoinduced process, undergoing oxidation and producing the electrons and protons required for the reaction series 5. The ESR and GC investigations show that cyclohexene oxidation occurs according to Eq. (6) and leads to the subsequent formation of dimeric species and allylic oxidation products.

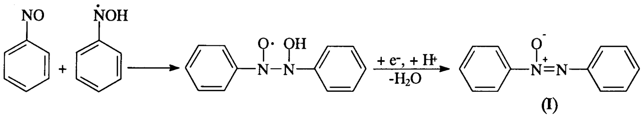


(5)



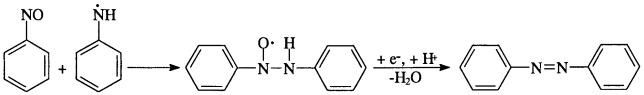
(6)

C_6H_5NO is a possible intermediate deriving from the photoinduced reduction of nitrobenzene. Since this nitroso-derivative is known to react easily with the radicalic intermediates reported in Eqs. (5) and (6), [21] it is expected to play a key role in the formation of all the detected stable products. Therefore, the ESR signals obtained in the absence of the spin trap nitrosodurene, can be tentatively ascribed to the formation of paramagnetic species deriving from the reactions of C_6H_5NO with $C_6H_5NOH^\bullet$, $C_6H_5NH^\bullet$, $C_6H_9{}^\bullet$. On the same basis, the reaction sequences of Eqs. (7) and (8) may explain the formation of (**I**) and (**II**), respectively.



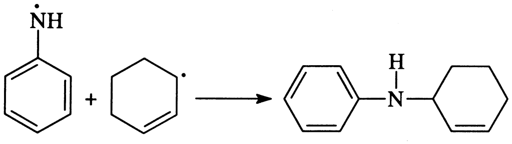
(**I**)

(7)



(**II**)

(8)



(**IV**)

(9)

The photoinduced allylic amination of cyclohexene with nitrobenzene to give (**IV**) may occur through reaction of Eq. (9) which involves radical intermediates deriving from both nitrobenzene reduction and cyclohexene oxidation. The reactant $C_6H_5NH^\bullet$ could be formed as a consequence of an attack of triplet phenylnitrene on cyclohexene. Allylic amination of unactivated alkenes with aromatic nitro-compounds is a process of high current interest, since allylamines are significant building blocks for the synthesis of numerous organic compounds which are important from a synthetic as well as from an industrial points of view [22]. In this framework, some of us have recently developed a new method for the catalytic synthesis of allylamines [18,23]. In that case, the process occurred at high temperature and pressure (160°C, 40 bar) and the reductant employed was CO.

When the nitrobenzene/cyclohexene mixture contained a powder suspension of TiO_2 or CdS or WO_3, nitrobenzene might be also reduced by the conduction band electrons of the irradiated semiconductor particles [4–10], and in line with previous investigations under aerobic conditions [13,24], the photogenerated positive holes could induce Reaction 6. Although any quantitative considerations about the relative contributions of the photochemical and the photocatalytic processes is not possible, the observation that the total amount of reduced nitrobenzene after 3 h irradiation did not depend significantly on the presence of the semiconductor allows us to conclude that efficiency of the two processes are comparable.

Table 1 shows that the presence of the semiconductor inhibited the allylic amination process which leads to the formation of (**IV**). This finding can be ascribed to competitive adsorption–desorption equilibria of the involved reagents and intermediates on the solid surface. In particular, high surface coverage by intermediates could reduce the possibility of encounter between the significant reactive moieties that would lead to (**IV**). Surface effects may also explain in part the significant effect of the semiconductor employed on the selectivity of the photocatalytic process. Another parameter affecting the product yields is the reducing power of the photoexcited semiconductor which follows the order $CdS>TiO_2>WO_3$ [11]. Accordingly, the highest amount of the totally reduced product (**III**) was obtained using powder suspensions of CdS.

As concluding remarks, we point out that, besides new mechanistic aspects, the results presented here indicate that both the photochemical and the photocatalytic approaches should be of interest to develop new synthetic routes in mild temperature and pressure conditions. In particular, the comparative investigation shows that it is possible to direct the photoprocesses towards the accumulation of different products.

Various reduction products of nitrobenzene can be obtained depending on the nature of the semiconductor employed with a selectivity higher than 40%. Upon direct irradiation of the nitro-compound, we achieve the goal of generating reactive intermediates of cyclohexene which take part in the formation of a useful product. In this way, it is possible to obtain the important building block $C_6H_5N(H)C_6H_9$. Further studies are in progress to optimise the described amination photoprocess and to establish possible developments in solar-driven formation of C–N bonds from unactivated substrates on a preparative scale.

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