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Photocatalytic formation of a carbamate through ethanol-assisted carbonylation of *p*-nitrotoluene†

Andrea Maldotti,*[a] Rossano Amadelli,[a] Luca Samiolo,[a] Alessandra Molinari,[a] Andrea Penoni,[b] Stefano Tollari[b] and Sergio Cenini[c]

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The nitroarene *p*-nitrotoluene is converted with a selectivity higher than 85% to the corresponding carbamate at room temperature and atmospheric pressure, using photoexcited particles of TiO_2 as catalyst and EtOH as carbonylating species.

Aromatic isocyanates are important intermediates in fine and industrial chemistry, which are currently prepared by reduction and phosgenation of the corresponding nitroarene.[1] A possible synthetic route to produce these compounds in the absence of phosgene, which is a poisonous and corrosive gas, is the reductive carbonylation of nitroarenes with CO (eqn. (1)).[2–5] This process may be also carried out in the presence of an alcohol (ROH) in order to produce carbamates that can be subsequently cracked into isocyanates (eqn. (2)).

$$\mathrm{ArNO_2 + 3CO \xrightarrow{catalyst} ArNCO + 2CO_2} \qquad (1)$$

$$\mathrm{ArNO_2 + 3CO + ROH \xrightarrow{catalyst} ArNHCOOR + 2CO_2} \qquad (2)$$

In this communication we present, as a preliminary account, a novel and simple approach for the conversion of *p*-nitrotoluene to the corresponding carbamate, using photoexcited particles of commercial TiO_2 as catalyst and EtOH instead of CO as carbonylating species (eqn. (3)). This photocatalytic reaction is carried out in mild temperature and pressure conditions irradiating with light of the near ultraviolet.

$$\underset{\mathbf{1}}{2p\text{-}\mathrm{CH_3\text{-}C_6H_4\text{-}NO_2}} + \mathrm{3C_2H_5OH} \xrightarrow[\substack{\mathrm{TiO_2},\ h\nu,\\ 25\,^{\circ}\mathrm{C},\ 760\ \mathrm{Torr}}]{} \underset{\mathbf{2}}{2p\text{-}\mathrm{CH_3\text{-}C_6H_4NHCO_2C_2H_5}} + \mathrm{3H_2O} \qquad (3)$$

Studies focusing on the use of semiconductors such as TiO_2 as heterogeneous photocatalysts have attracted considerable interest in the field of "green chemical processes", where one seeks a high efficiency and selectivity under mild and environment-friendly conditions.[6] Photoexcitation of TiO_2 particles at wavelengths corresponding to the band gap value promotes electrons in the conduction band leaving positive holes in the valence band. If electrons and holes can reach the surface of the semiconductor before recombination takes place, they can induce redox processes of organic substrates. Here, in the absence of O_2, conduction band electrons are expected to reduce the nitroarene **1**,[7,8] while the powerful oxidizing properties of the photogenerated holes should lead to the oxidation of the employed alcohol to CO_2 and H_2O with the possible involvement of adsorbed $OH^{\bullet}$ radicals.[9,10]

A typical photocatalytic experiment[11] was carried out irradiating with light of wavelength higher than 380 nm deaerated powder dispersions of TiO_2 (3 g dm^{-3}, Degussa P25) suspended in *p*-nitrotoluene (3.0×10^{-2} mol dm^{-3}) containing mixtures of EtOH/ CH_3CN (3 : 7 v/v). The gas chromatographic analysis revealed that 7% of **1** disappeared after 8 h of photoexcitation at 25 ± 1 °C and 760 Torr of N_2. The main product was the carbamate **2** with only minor amounts of *p*-toluidine **3**, by comparison with the retention times of those of authentic samples and by co-injection with the authentic compounds. Specifically, the gas chromatographic analysis showed that the carbamate was obtained with 75% selectivity and that the detected products represented more than 90% of the converted *p*-nitrotoluene. Control experiments demonstrated that **1** did not undergo any reaction in the absence of TiO_2 or without irradiation. The carbamate **2** was prepared as standard for the gas chromatographic analyses following a previously reported procedure.[12,13]

It is reasonable to ascribe the described photocatalytic carbonylation of the nitroarene **1** to different cross reactions involving some of the reactive species originated from sequential monoelectronic redox processes induced by the semiconductor. Several transient reactive species, including nitroso and nitrene derivatives, may originate from the conduction-band-assisted reduction of **1**. Other reactive intermediates are expected to be formed as a consequence of the simultaneous hole-assisted oxidation of EtOH, as briefly discussed in the following. The involvement of the initial reagents **1** and EtOH in the overall process is also plausible.

The TiO_2-assisted oxidation of EtOH has been experimentally followed by infrared spectroscopy. Thin films of TiO_2 deposited on glass supports were irradiated in the bottom of a 10 cm length infrared gas cell containing air saturated with vapours of EtOH. Photochemical excitation of this film caused a significant decrease of some absorptions typical of EtOH in the gas phase: 2800–3000 cm^{-1}, 1050–1100 cm^{-1}. The simultaneous growing of new bands in the 1700–1800 cm^{-1} range indicated that EtOH was partially converted to carbonylic derivatives. The formation of a new absorption at 2720 cm^{-1} typical of aldehydic C–H bonds is a clear indication of the presence of acetaldehyde among these products. Photochemical excitation was also accompanied by the formation of CO_2, as shown by the growth of its typical absorptions at 2350 cm^{-1} and 660 cm^{-1}.

Although we do not have infrared evidence of CO formation, there is reason to expect that this compound is a relevant

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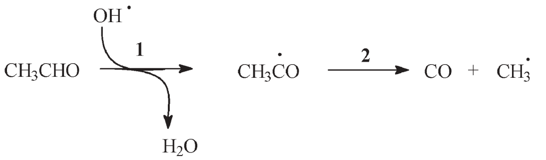
† Electronic Supplementary Information (ESI) available: IR spectra. See http://www.rsc.org/suppdata/cc/b4/b418571d/
*mla@dns.unife.it

intermediate in the photocatalytic system. Indeed, in one oxidation route, photogenerated $OH^{\bullet}$ radicals can abstract formyl hydrogens from acetaldehyde yielding acyl radicals (first step in eqn. (4)).[14] These, in turn, are well known to undergo very fast decarbonylation according to the second step in eqn. (4). Gas chromatographic analysis provided evidence that addition of CO did not affect significantly yield and selectivity of the photocatalytic conversion of **1** to **2**, suggesting that the photogenerated CO, if it is involved, is likely to participate in the carbonylation process as an adsorbed species derived, in turn, from the adsorbed aldehyde.

Some additional experiments indicate that nature and reactivity of the employed hole-scavenger had a pronounced influence on the selectivity of the photocatalytic process. In fact, with MeOH as photooxidizable substrate instead of EtOH, the amine **3** was the only observable photoproduct of **1**. Other experiments showed that also in the presence of 2-PrOH the photoinduced reduction of **1** proceeded mainly to amine formation: 85% of **3**, 15% of **2**. A plausible explanation is that both MeOH and 2-PrOH produce lower amounts of CO in comparison to EtOH. Indeed, hydrogen atom abstraction from formaldehyde (from MeOH oxidation) is comparatively more difficult than from acetaldehyde (eqn. (4), step 1). Moreover, further oxidation of acetone (from 2-PrOH) can lead to $CH_3COCH_2^{\bullet}$ radicals which are known to yield substantial amounts of ketene (CH_2CO) instead of CO[15].



(4)

The peculiar reactivity of EtOH has prompted us to carry on photocatalytic experiments in neat EtOH. It is seen in Fig. 1 that the formation of both **2** and **3** follows a zero-order kinetics, indicating that consecutive reactions can be ruled out. It is noteworthy that the use of neat ethanol as dispersing medium enhances both efficiency and selectivity of the photocatalytic process. In particular, it is seen that: (i) the overall rate of conversion of **1** (about 13%) almost doubles with respect to the experiments carried out in mixed solvent; (ii) the conversion rate of **1** does not decrease significantly during the 8 h of the experiment; (iii) the carbamate **2** is obtained with about 85% selectivity.

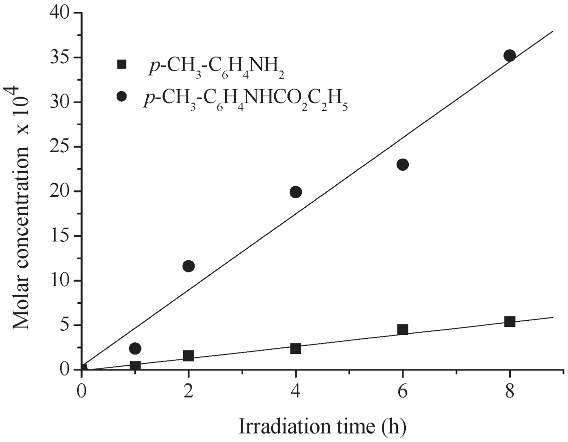


Fig. 1 Formation of **2** and **3** upon irradiation ($\lambda > 380$ nm) of TiO_2 (3 g dm^{-3}) dispersed in deaerated *p*-nitrotoluene (3.0×10^{-2} mol dm^{-3}) containing EtOH.

In this work, *p*-nitrotoluene has been chosen as a substrate because, in the given experimental conditions, it undergoes neither direct photochemical reactions, nor facile redox processes of the *para*-substituent methyl group. These requirements set the limits to the choice of other nitroarenes, and appropriate experimental conditions for further investigations should comply with these criteria. Thus, for example, *p*-nitrobenzaldehyde does not appear to be a suitable substrate since we verified that both functional groups undergo reduction at photoexcited TiO_2, thus severely complicating the overall process.

In conclusion, this work describes optimal conditions in which the reactive species generated both from the conduction-band electrons and from the valence-band positive holes are precursors of carbamate formation. The described reaction is a new appealing synthetic route in applied organic chemistry, since it may produce very important chemicals such as carbamates with good selectivity and without using harmful reagents such as phosgene and CO. In particular, we achieve the goal of generating carbonylating species *in situ* from EtOH in mild temperature and pressure conditions using an inexpensive photocatalyst that combines unique characteristics, such as stability and environmental tolerance. In order to rationalize the drastic influence of alcohol on the activity of TiO_2, more experiments are needed.

This completely new photochemical activity of TiO_2 is of general interest in the field of photocatalysis. In fact, we definitely confirm that suitable experimental conditions can be found in order to control the well known powerful reactivity of TiO_2 which, therefore, can be successfully employed also for synthetic purposes in addition to environmental decontamination. Further studies are also in progress to establish the possible employment of other semiconducting compounds able to utilize the visible light for the exploitation of solar light. Future developments will also have to take into account the effect of other substituents on the nitroarene.

Andrea Maldotti,*[a] Rossano Amadelli,[a] Luca Samiolo,[a]
Alessandra Molinari,[a] Andrea Penoni,[b] Stefano Tollari[b] and
Sergio Cenini[c]
[a]*Dipartimento di Chimica, Sezione ISOF –CNR, Università di Ferrara, Via L. Borsari 46, 44100, Ferrara, Italy. E-mail: mla@dns.unife.it*
[b]*Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, Via Valleggio 11, 22100, Como, Italy*
[c]*Dipartimento di Chimica Inorganica Metallorganica e Analitica, I.S.T.M.- C.N.R., Università di Milano, Via G. Venezian 21, 20133, Milano, Italy*

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