Photoinduced Reduction of Nitro Compounds on Semiconductor Particles

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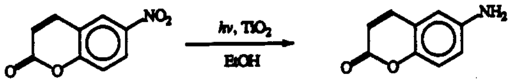
Irradiation of a wide band gap semiconductor (SC) promotes one electron from the valence band (VB) to the conduction band (CB). The excited state of the SC can be expressed as SC(e^-, h^+).[1] The electron in the conduction band is readily available for transference while the electron hole in the valence band is open for donation.[2] A reactant that receives the electron from SC would be reduced, while a reactant that donates an electron to SC would be oxidized. On the basis of this principle, a variety of redox reactions can be catalyzed by semiconductors upon irradiation. Although photoinduced oxidation of organic compounds on semiconductor particles has been fruitfully investigated,[3] there are only a few reports on the reduction of organic compounds.[4] Here we report the photoinduced reduction of aromatic and aliphatic nitro compounds using TiO_2 as a catalyst.

Results and Discussion

Irradiation of a suspension of titanium dioxide (anatase) in ethanol containing 6-nitrocoumarin gives 6-aminocoumarin, acetaldehyde, and hydrogen (eq 1). The suspension is filtered, and the aminocoumarin is isolated in 79% yield. The procedure is much simpler than any other literature procedures for the preparation of this aminocoumarin from its nitro compound.[5] To the best of our knowledge, this is the first example of a photoinduced reduction of nitro compounds on a semiconductor. This photoinduced reduction scheme is also applicable to a wide variety of nitro compounds (eqs 2-4). In all cases, the yields are very high (Table I).

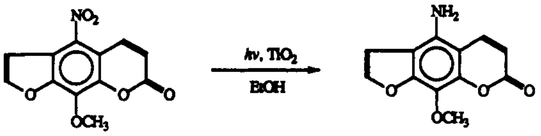


(1)

Table I. Photoinduced Reduction of Nitro Compounds on TiO_2 Particles

reactant	product	yields[a] (%)
6-nitrocoumarin	6-aminocoumarin	79[b]
5-nitro-8-methoxypsoralen	6-aminopsoralen	85
1-nitronaphthalene	1-aminonaphthalene	77
9-nitroanthracene	9-aminoanthracene	85
1,4-dinitrobenzene	4-nitroaniline	92
4-nitroacetophenone	4-aminoacetophenone	85[b]
4-nitroacetophenone	4-aminoacetophenone	87
4-nitroacetophenone	4-aminoacetophenone	88[c]
3-nitroacetophenone	3-aminoacetophenone	92
4-nitrotoluene	4-aminotoluene	85
4-nitroanisole	4-methoxyaniline	45[d]
12-nitrododecanoic acid	12-aminododecanoic acid	89[e]

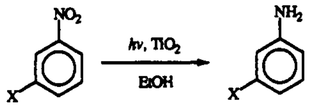
[a] Yield determined by HPLC unless indicated otherwise, typical percentage error ±2%. Photolysis time = 15 min unless indicated otherwise. [b] Yield determined by isolation, typical percentage error ±5%. [c] Recycled TiO_2 particles were reused for the fourth time. [d] Mass balanced with remaining starting nitro compound. [e] Photolyzed for 150 min.



(2)

(3)

X = H, CHO, $COCH_3$, CN, CH_3, OCH_3



(4)

X = $CH{=}CH_2$, $COCH_3$

It is known that the electron hole in the valence band of an excited semiconductor can cause oxidation of an alcohol to give a corresponding carbonyl compound, hydrogen, and a proton as illustrated in Figure 1.[6] Therefore, it is possible that the reduction of a nitro compound is caused by the hydrogen produced during oxidation of the solvent. In a control experiment, a suspension containing TiO_2 and *p*-nitroacetophenone was saturated with hydrogen. The nitro compound was not reduced under this condition. For most nitro compounds, direct irradiation with a 350-nm light in the absence of TiO_2 does not produce any significant amount of reduction product. For example, direct irradiation of a solution of *p*-nitroacetophenone in the absence of TiO_2 does not lead to the formation of any Norrish-type photoproduct or *p*-aminoacetophenone, whereas the nitro compound is completely reduced to its amino derivative within 15 min in the presence of TiO_2. It has been reported that irradiation of 9-nitroanthracence in ethanol results in a nitrite isomer that decomposes to give 9,10-anthraquinone as a major product (eq 5).[7] Irradiation of a TiO_2 suspension

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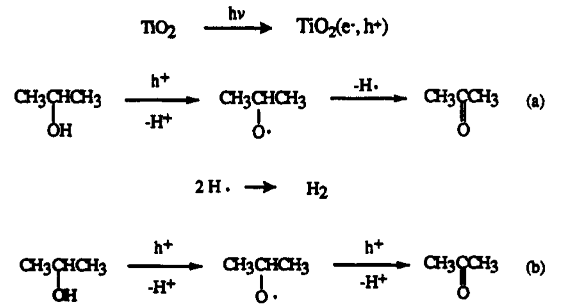


Figure 1. Oxidation of alcohol on semiconductor particles.

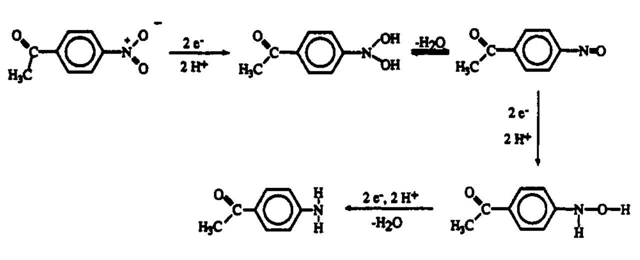
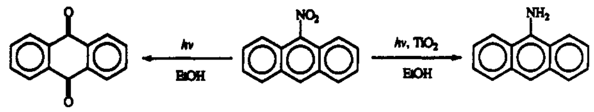


Figure 2. Reductions of nitro compounds on semiconductor particles.


(5)

containing 9-nitroanthracene in ethanol produces 9-aminoanthracene, a reduction product instead.

The efficiency for the reduction is generally increased when the concentration of a nitro compound decreases. The analyses based on the UV–vis absorption spectra of nitro compound solutions and TiO_2 suspensions indicate that the photoreduction occurs only when light is absorbed by the semiconductor. The photoredox reactions are halted when photons are predominantly absorbed by the nitro compounds. This concentration limit is dependent on the extinction coefficient of a nitro compound in the UV region. For example, it is 5×10^{-3} M for 6-nitrocoumarin and 5×10^{-2} M for *p*-nitrobenzaldehyde and *p*-nitrotoluene. These findings confirm that the photoinduced reduction is initiated by the illuminated SC.

Similar to the mechanism for an electrochemical reduction of a nitro compound,[8,9] photoinduced six-electron reduction can be illustrated as in Figure 2 in which sequential electron transfers, protonations, and dehydration occur. A complete reduction of a nitro compound would require six protons and leave the same numbers of electron holes behind. If all of these electron holes are used to oxidize alcohol solvent according to a scheme illustrated in Figure 1a or 1b, six protons would be produced. Our experimental results show that the pH of the suspension does not change noticeably after the irradiation. The oxidation of an alcoholic solvent and the reduction of the nitro compounds are therefore coupled. If the photoinduced reduction of a nitro compound is coupled with an oxidation of 2-propanol as illustrated in Figure 1a, the stoichiometrical ratio of nitro compound reduction to acetone formation should be six (eq 6). If the reduction is coupled with an oxidation as illustrated in Figure 1b, the ratio should be 3 (eq 7). Although both

$$RNO_2 + 6(CH_3)_2CHOH \rightarrow RNH_2 + 6(CH_3)_2C{=}O + 2H_2O + 3H_2 \quad (6)$$

$$RNO_2 + 3(CH_3)_2CHOH \rightarrow RNH_2 + 3(CH_3)_2C{=}O + 2H_2O \quad (7)$$

oxidation processes, as in 1a and 1b, give 1 equiv of proton per electron hole, the sequence in 1b does not offer any molecular hydrogen. It is found that the molar ratio of acetone formation to *p*-nitroacetophenone reduction is 5.3 throughout the reduction period. Therefore, the oxidation primarily follows the mechanism illustrated in Figure 1a. This is consistent with the observations of hydrogen gas in this study and other literature reports.[3]

The reduction efficiency is related to the reduction potentials of the nitro compounds. It is found that a nitro compound with reduction potential well below the conduction band energy of TiO_2 (−0.85 eV vs SCE)[2] is more reducible than those with higher reduction potentials. For example, it takes less than 15 min to reduce *p*-nitroacetophenone (−0.1 eV) quantitatively in a TiO_2 suspension, while it requires 30 min for *p*-nitroanisole (−0.35 eV) and 3 h for an aliphatic nitro compound such as 12-nitrododecanoic acid (−0.8 eV). Due to the significant differences in their reduction potentials, 1,4-dinitrobenzene (−0.17 eV) can be quantitatively reduced to *p*-nitroaniline (−0.35 eV)[10] (Table I). Similarly, the nitro group is reduced before other functional groups such as aceto, ester, cyano, and even aldehyde in a multifunctional compound. These latter functional groups have much higher reduction potentials.

According to the reaction mechanism illustrated in Figure 2, the reduction efficiency is influenced by a series of processes and factors including the electron transfer from the conduction band of TiO_2 to a nitro compound, the back-electron transfer from a nitro radical anion to the valance band, and proton availability. The electron-transfer processes are in competition with the fast electron–electron hole recombination within the semiconductor. The recombination within the semiconductor and the back-electron transfer from the nitro radical anion can presumably be retarded by the addition of an external electron-donating agent such as an amine. According to a previous study, addition of such an electron donor increases the efficiency of the reduction from benzaldehyde to benzyl alcohol on TiO_2.[11] However, our present study shows that addition of an electron donor, such as diisopropylamine (0.1–1.0 M), actually reduces the efficiency noticeably (Table II). These findings indicate that the electron transfer from SC to the nitro compound is so fast and the back-electron transfer from the nitro radical anion to SC is so slow that an additional electron donor does not influence these processes significantly. Thus, the amine acts only as a base that reduces the proton availability, which in turn reduces the overall efficiency for the reduction.

A comparison between this photoinduced approach and some other conventional methods have been made by using

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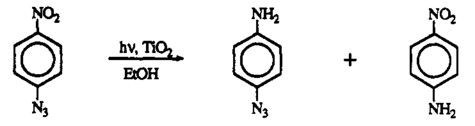
Table II. Reduction of *p*-Nitroacetophenone on Semiconductor Particles

condns (solvent, time (min))	*p*-nitroacetophenone[d] (%)	*p*-acetophenylhydroxylamine[d] (%)	*p*-acetoaniline[d] (%)
EtOH, 0	100	0	0
EtOH, 1	53	31	16
EtOH, 2	40	28	31
EtOH, 3	30	27	42
EtOH, 15	0	0	99
EtOH,[a] 15	55	28	13
EtOH,[b] 15	66	24	10
EtOH,[c] 15	0	0	99
MeOH,[c] 15	0	14	85
IPA,[c] 15	4	12	79

[a] 0.1 M diisopropylamine added. [b] 1.0 M diisopropylamine added. [c] Anhydrous solvent. [d] Typical percentage error ±5%.

3-nitrostyrene and 4-nicotinamidonitrobenzene. Reduction of 4-nicotinamidonitrobenzene with $Sn/SnCl_2$ in strong acid causes partial hydrolysis of the amide linkage. However, photoinduced reduction offers a clean reduction with high yield. In addition, catalytic hydrogenation of 3-nitrostyrene using Pd/C in ethanol gives 3-ethylaniline, a reduction of both nitro and vinyl functional groups, while TiO_2-catalyzed photoreduction gives 3-aminostyrene as the only product. In addition, the semiconductor particles used in this reduction process can be recycled by simple filtration and reused without losing their catalytic ability (Table I).

The photoinduced reduction of *p*-nitroacetophenone was studied at a shorter time interval. It is found that the reduction proceeded via a hydroxylamine intermediate (Table II, eq 8) that was confirmed by comparison with an independently prepared authentic sample.[12] A control experiment demonstrates that the hydroxylamine itself in the presence of illuminated TiO_2 gives its amino derivative. This finding further confirms the reaction mechanism proposed in Figure 2.



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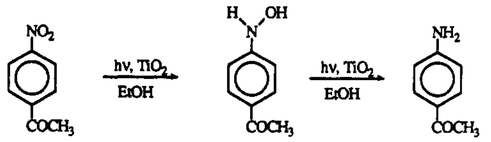

(9)

Experimental Section

Materials. *p*-Nitroanisole, *p*-nitrotoluene, *p*-nitroacetophenone, *m*-nitroacetophenone, *p*-dinitrobenzene, 9-nitroanthracene, 1-nitronaphthlene, 3-nitrostyrene, and *p*-nitrobenzaldehyde were obtained from Aldrich. Titanium dioxide (P-25 anatase) was obtained from DeGussa Corp. All reagent were used without further purification. 6-Nitrocoumarin, 5-nitro-8-methoxypsoralen, and 4-nicotinamidonitrobenzene were prepared according to literature procedures with minor modifications.[5,14] GC–MS spectra were obtained on a Hewlett-Packard Model 5890 series II gas chromatography with a Model 5917A mass spectrometer. All products were identified by GC–MS and confirmed by comparison with an authentic sample on a Hewlett-Packard 1050 series HPLC. Photolyses were carried out in a Rayonet photochemical reactor equipped with 350-nm bulbs.

General Procedure for Irradiation with TiO_2: Small Scale. In a 5-mL shell vial equipped with a magnetic stir bar, 2 mL of a 0.01 M solution of a nitro compound in 95% ethanol and 2 mL of a suspension of 5.0 g/L of TiO_2 in 95% ethanol were mixed. The vial was sealed with a rubber septum and purged with nitrogen for 5 min. The mixture was stirred and irradiated in a Rayonet photochemical reactor for 15 min. After the irradiation, the mixture was filtered with a 0.2-μm HPLC syringe filter to remove TiO_2 particles. The resulting solution was injected into the GC–MS and HPLC for product identification and yield measurement.

General Procedure for Irradiation with TiO_2: Preparative Scale. In a 500-mL round-bottom Pyrex flask equipped with a magnetic stir bar were mixed 200 mL of a 0.01 M solution of nitro compounds in 95% ethanol and 200 mL of a suspension of 5.0 g/L of TiO_2 in 95% ethanol. The flask was sealed with a rubber septum and purged with nitrogen for 50 min. The mixture was stirred and irradiated in a Rayonet photochemical reactor equipped with GE FBT5-BLB black light (350-nm) bulbs for 150 min. After the irradiation, the mixture was centrifuged and then filtered with a 0.2-μm ANOPORE filter to remove TiO_2 particles. The solution was injected into the GC–MS and HPLC for product identification. The solvent was removed, and the product was recrystallized. The yields were determined gravimetrically. The semiconductor particles can be recycled by simple filtration and reused without losing their catalytic ability.

Percent Yield Determination. Six solutions of known concentrations of the nitro compound and product ranging from 0.001–0.005 were analyzed using HPLC. Area ratios were then determined. From these data, concentrations of reactant and product were determined after irradiation. The yield determination for *p*-acetophenyl hydroxyl amine is carried out by assuming its extinction coefficient is the same as that of *p*-acetoaniline.

Detection of Hydrogen and Carbonyl Compound Formation. Hydrogen gas produced from the irradiation of a TiO_2 suspension was analyzed with a hydrogenation experiment. The experimental apparatus has been described elsewhere.[11] The carbonyl compounds generated from the oxidation of alcohol solvents were identified with GC by comparison with their authentic samples. Stoichiometric determination of acetone formation and *p*-nitroacetophenone reduction was carried out in a 2-propanol suspension of TiO_2 (2.5 g/L) containing *p*-nitroacetophenone (2.5×10^{-3}). The suspension was irradiated, and samples were drawn periodically and analyzed on a Hewlett Packard GC with an FID detector. The molar ratios of the acetone formation of *p*-nitroacetophenone reduction were then calculated according to the calibration curves using corresponding authentic samples.

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