Heterogeneous Photocatalytic Reactions of Azobenzenes on Titanium Dioxide Powder in Methanolic Solution

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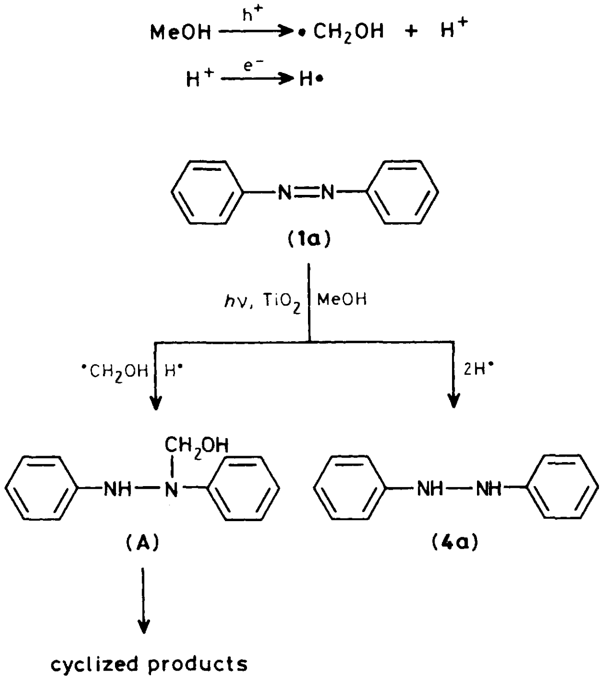
Irradiation of a TiO_2 powder suspension in a methanolic solution of an azobenzene results in the formation of 1,2,4-triphenyl-1,2,4-triazolidines and a 2-phenylindazole in moderate yields.

Increasing attention has been recently paid to photocatalytic processes occurring on particulate semiconductors suspended in solution.[1] In photocatalytic reactions, effective utilization of radical intermediates formed by reactions with carriers photogenerated in semiconductor particles would be a useful synthetic process. Here we report the photocatalytic reactions of azobenzenes in methanolic solution in the presence of TiO_2 powder.

Anatase TiO_2 powders (Special grade, Wako Pure Chemical Industries Ltd.) were used without further treatment unless otherwise stated. The powder (20 mg) was added to a methanolic solution of an azobenzene (5.0 mg, 2.7×10^{-2} mmol) in a Pyrex tube, and the mixture was sonicated for 5 min. The suspension was then externally irradiated with a 300 W high-pressure Hg arc lamp with stirring.

By this means, azobenzene itself (in air) afforded 1,2,4-triphenyl-1,2,4-triazolidine (**2a**) (45%) and 2-phenylindazole (**3a**) (trace) in addition to small amounts of oxygenation products [(**5a**), azoxybenzene, and 2-hydroxyazobenzene] (Table 1). When platinized (7%) TiO_2 photocatalysts were used (prepared by carrying out photocatalytic reaction in K_2PtCl_6-containing ethanol[2]), in contrast, neither (**2a**) nor (**3a**) was obtained but degradation products were detected. This might be attributed to the reducibility of Pt sites on a

TiO_2 particle being too great. Products of experiments with various 4-substituted azobenzenes are summarized in Table 1. The structures of (**2**) and (**3**) were determined on the basis of ^1H and ^{13}C n.m.r., i.r. spectroscopy, and mass spectrometry. In the case of 4-methylazobenzene (**1b**), the main product was (**2b**); this behaviour corresponds to that of unsubstituted azobenzene. In the case of 4-chloroazobenzene (**1c**), however, the yield of 1,2,4-triazolidine (**2c**) was lower; this is attributable to photoinduced dechlorination. The reaction of (**1b**) affords two kinds of 1,2,4-triazolidine (monomethyl and dimethyl), while that of (**1c**) gives only monochloro compound. On the other hand, the reaction of the *p*-alkoxyazobenzenes (**1d** and **e**) yielded selectively the corresponding 2-phenylindazoles (**3d** and **e**), respectively. Thus the product ratio of (**2**) and (**3**) varies greatly with substituent group.



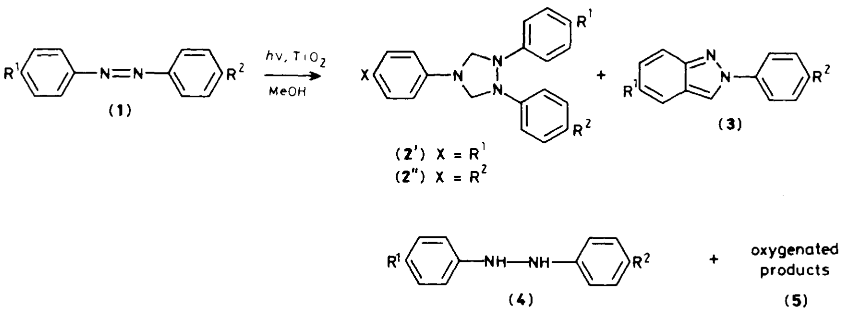
Scheme 1

In argon-purged methanolic solutions of azobenzenes, quite different results were obtained. The azo compounds (**1a**—**c**) were converted into hydrazo compounds by irradiation for 4—6 h. Further irradiation did not lead to 1,2,4-triphenyl-1,2,4-triazolidine. Such clear differences in reactions in air and in argon indicate that dissolved oxygen plays a decisive role; thus might afford superoxide ion by reaction with photogenerated electrons. The reaction of the alkoxy derivatives (**1d**—**g**), on the other hand, gave 2-phenylindazoles in good yields.

In the absence of TiO_2 powder, in all these reactions, no such products were detected.

In order to elucidate the reaction paths, the energy levels of TiO_2 and the solution species (methanol and azobenzenes) were estimated. In these experiments, a single crystal of TiO_2 (rutile) annealed in hydrogen atmosphere was used. The flat-band potential of this electrode in methanolic solution was determined to be -1.45 V (*vs.* Ag/Ag^+) from the onset potential for anodic photocurrent and Mott-Schottky plots of the interfacial capacitance. The valence band-edge of a single-crystal TiO_2 electrode could then be estimated as about 1.5 V (*vs.* Ag/Ag^+) in this solution. It was impossible, however, to determine the oxidation potential of azobenzenes (**1a** and **d**) in this solution, since a large anodic current due to the oxidation of methanol flows at 0.6 V (*vs.* Ag/Ag^+). We

Table 1. Heterogeneous photocatalytic reactions of azobenzenes on TiO_2 powder in methanolic solution.



Run	Compounds			Atmosphere	Irradiation time (h)	Yields[b] (%)			
	No.	R^1	R^2			(**2**)[(**2'**):(**2''**)]	(**3**)	(**4**)	(**5**)[a]
1	(**1a**)	H	H	Air	24	45	Trace	0	17
2				Ar	6	0	0	69	0
3	(**1b**)	Me	H	Air	24	45 (1 : 1)	Trace	0	5
4				Ar	6	0	0	95	0
5[c]	(**1c**)	Cl	H	Air	24	27 (0 : 1)	Trace	0	Trace
6				Ar	4	0	0	92	0
7	(**1d**)	MeO	H	Air	24	0	47	0	12
8				Ar	6	0	53	0	0
9	(**1e**)	EtO	H	Air	24	0	22	0	12
10				Ar	6	0	70	0	0
11	(**1f**)	MeO	Me	Ar	6	0	69	0	0
12	(**1g**)	MeO	MeO	Ar	6	0	61	0	0

[a] Azoxybenzenes and 2-hydroxyazobenzenes produced by photo-Wallach rearrangement of azobenzenes. [b] Yields determined by g.l.c. [c] As by-product, azobenzene (9%) and unsubstituted 1,2,4-triphenyl-1,2,4-triazolidine (17%) were produced.

therefore adopted values [1.4 V *vs.* Ag/Ag$^+$ for (**1a**) and 1.3 V *vs.* Ag/Ag$^+$ for (**1d**)] determined by cyclic voltammetry in acetonitrile solution. Assuming that powdered TiO_2 used in our experiments has nearly the same energy diagram as a single crystal of TiO_2 (though there might be a small difference between anatase and rutile in the energy scheme[3]), it follows that the oxidation of azobenzenes to the corresponding radicals by photogenerated 'holes' is thermodynamically feasible. In the present system, however, judging from the obtained products and the oxidation potentials of the substrates, it is reasonable to assume that methanol is oxidized preferentially to a hydroxymethyl radical.[4] Then a possible reaction mechanism is that illustrated in Scheme 1. The first step is the creation of an electron–hole pair within the illuminated TiO_2 particle. The hole (h^+) oxidizes methanol, forming a hydroxymethyl radical and a proton. The proton is reduced by the electron (e^-) to form a hydrogen radical. The hydroxymethyl radical and the hydrogen radical thus formed should attack azobenzene adsorbed on TiO_2 powder to form a hydroxymethyl adduct (**A**). This intermediate (**A**) could then be dehydrated and cyclized to a 1,2,4-triazolidine or an indazole. The mechanism of the substituent effect is under study.

In conclusion, we have demonstrated that 1,2,4-triphenyl-1,2,4-triazolidines and 2-phenylindazoles can be synthesized in moderate yields by photocatalytic reactions of methanolic solutions of azobenzenes in the presence of TiO_2 powder, and that product selectivity can be achieved by varying the substituent.

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References

1 For example, M. A. Fox, *Top. Curr. Chem.*, 1987, **142**, 71.
2 B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, 1978, **100**, 4317.
3 H. Minoura, M. Nasu, and Y. Takahashi, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 1064.
4 H. Gerischer, *Surface Sci.*, 1969, **14**, 97.