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Oxygenation of Aldimines and Deoxygenation of Nitrones on Irradiated TiO_2

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Abstract: While aldimines have been selectively oxidized to nitrones in TiO_2 suspended acetonitrile solution in the presence of O_2 upon irradiation, nitrones are reduced to their deoxygenated derivatives with retention of C=N by TiO_2 photocatalysis under a nitrogen atmosphere. © 1998 Elsevier Science Ltd. All rights reserved.

Heterogeneous photocatalytic processes employing semiconductor oxides have attracted the attention of several chemists. Because of its high photoactivity and chemical stability, TiO_2 is being extensively used in various photoredox reactions.[1-3] Several groups are investigating ways of using TiO_2 photocatalyst in harnessing solar energy, organic synthesis and abating air and water pollution.

Our earlier studies with TiO_2 as the photocatalyst revealed that in the presence of oxygen, arylsulfenylacetic acids and arylsulfinylacetic acids undergo S-oxidation with retention of COOH group.[4] We have also established that while arylsulfonylacetic acids give their deoxygenated derivatives without decarboxylation on irradiated TiO_2 in the presence of nitrogen,[4] aryl methyl and dialkyl sulfones are reduced to the corresponding sulfoxides and sulfides[5] and triaryl phosphine oxide to triaryl phosphine[6] under the same conditions.

Though there is no report on the direct oxidation of aldimines to nitrones, deoxygenation of nitrones into aldimines has been reported. The photosensitized electron transfer reactions of nitrones resulted in deoxygenation to give imines along with the ketonic products.[7] Triphenylphosphine has also been employed

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for the deoxygenation of nitrones.[8] Our continued interest in site selective organic redox reactions prompted us to investigate oxidation of aldimines and reduction of nitrones.

All aldimines and nitrones were prepared as reported.[9] TiO_2 (Aldrich) sample with 99.9% purity was used. One millimolar solution of aldimine or nitrone in acetonitrile (5ml) containing particulate TiO_2 (1%) was irradiated using a Semi-micro photochemical reactor (Photochemical Reactors Ltd., UK) with 6W medium pressure mercury vapour lamp ($\lambda \geq 350$nm). The products were characterised by gas chromatograph (Netel, India) fitted with OV-1 column and FID.

Bandgap irradiation of TiO_2 promotes an electron from its valence band (V_B) to the conduction band (C_B)[1-3] leaving the electron hole (h^+) in theV_B. In reduction reactions, an electron in the C_B combines with the surface adsorbed substrate to give a radical anion. The hole (h^+) in the V_B is ready to accept an electron from the surface bound substrate producing a radical cation during oxidation. In the presence of oxygen, it has been well established that superoxide ($O_2^{\cdot-}$) will be formed by capturing C_B electron. Being a powerful oxidising agent, $O_2^{\cdot-}$ oxidises the surface adsorbed organic substrate. Under a nitrogen atmosphere, an electron is transferred from C_B to the organic substrate. The band edge positions of the C_B and V_B redox potential levels of the substrates determine the probability and rate of charge transfer processes for electrons and holes.[2] The surface of TiO_2 has very high oxidation potential (3.02 V) which is considerably higher than that of conventional oxidising agents like chlorine (1.36 V) and ozone (2.07 V) and therefore TiO_2 is capable of bringing about oxidation of many organic compounds. The oxidation potentials of aldimines are found to be well below that of TiO_2 (see Table 1).

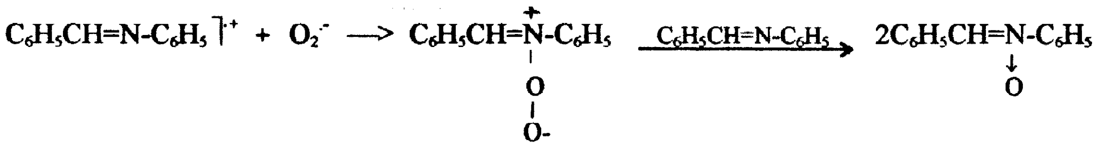
When an acetonitrile solution of aldimine is irradiated in the presence of suspended TiO_2 and oxygen, the corresponding nitrone is formed in ≥ 70% without affecting the C=N along with small amounts of aldehydes, hydroxylamines and amines (low boiling compounds) and carboxylic acids and diazo compounds (high boiling compounds). In Table 1 the yields of various products are shown. The following mechanism (Scheme 1) is proposed for the oxidation.

Oxidation

$$TiO_2 \xrightarrow{h\nu} TiO_2\,(h^+) + e^- \quad (1)$$

$$O_2 + e^- \longrightarrow O_2^{\cdot-} \quad (2)$$

$$C_6H_5CH{=}N{-}C_6H_5 + TiO_2\,(h^+) \longrightarrow [C_6H_5CH{=}N{-}C_6H_5]^{\cdot+} + TiO_2 \quad (3)$$



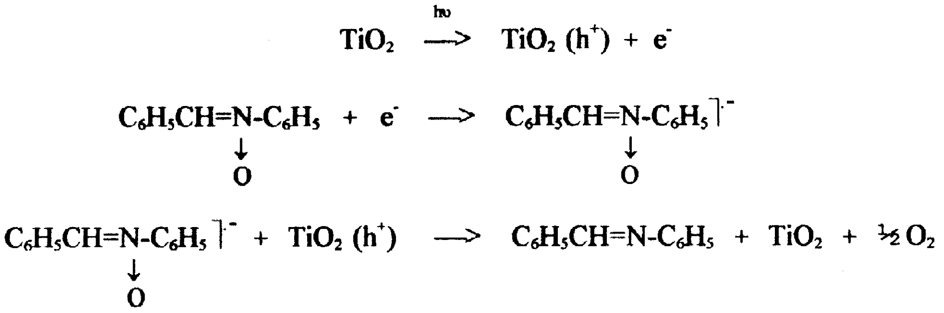
$$C_6H_5CH{=}N{-}C_6H_5]^{\cdot +} + O_2^{\cdot -} \longrightarrow C_6H_5CH{=}\underset{\substack{| \\ O \\ | \\ O^-}}{\overset{+}{N}}{-}C_6H_5 \xrightarrow{C_6H_5CH=N-C_6H_5} 2C_6H_5CH{=}\underset{\substack{\downarrow \\ O}}{N}{-}C_6H_5 \qquad (4)$$

Scheme 1

If the above mechanism is true, an electron-donating substituent present in the phenyl ring of the aldimine will favour step (3) which involves electron transfer and an electron-withdrawing substituent will less favour this. Indeed the yield of nitrone is more with 4-methoxybenzylideneaniline (88%) than with 4-chlorobenzylideneaniline (69%, Table 1).

TiO_2 photocatalyzed reduction of acetonitrile solutions of α-aryl-N-phenyl nitrones have been carried out in the presence of nitrogen and the process resulted in the formation of aldimines in good yields without affecting C=N (Table 2). The mechanism proposed for the reduction of nitrones (Scheme 2) is analogous to that proposed for the reduction of the sulfonyl group in sulfones[4,5] and other reductions[6] studied by us.

Reduction



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

$$C_6H_5CH{=}\underset{\substack{\downarrow \\ O}}{N}{-}C_6H_5 + e^- \longrightarrow C_6H_5CH{=}\underset{\substack{\downarrow \\ O}}{N}{-}C_6H_5]^{\cdot -}$$

$$C_6H_5CH{=}\underset{\substack{\downarrow \\ O}}{N}{-}C_6H_5]^{\cdot -} + TiO_2\,(h^+) \longrightarrow C_6H_5CH{=}N{-}C_6H_5 + TiO_2 + \tfrac{1}{2}O_2$$

Scheme 2

When irradiations were carried out with 64W multilamp reactor (λ ≥ 366nm) or 400W annular reactor (λ ≥ 350nm) for 30 min, in both oxidation and reduction reactions more of low boiling and high boiling compounds were obtained with the cleavage of C=N bond.

Thus it is possible to achieve the selective oxidation of aldimines to nitrones and reduction of the N-O bond of nitrones without affecting C=N in the two systems with TiO_2 as the photocatalyst under mild conditions.

Table 1. Photocatalyzed Oxidation[a] of Aldimines [p-R-$C_6H_4CH{=}NC_6H_5$] on TiO_2

R	N	A	X_1	X_2
H (0.94 V)	93	2	3	2
OCH_3 (0.86 V)	88	3	4	5
CH_3 (0.91 V)	87	5	4	4
Cl (0.93 V)	69	14	3	14
Br (0.96 V)	71	11	5	13

Table 2. Photocatalyzed Reduction[b] of Nitrones [p-R-$C_6H_4CH{=}N(O)C_6H_5$] on TiO_2

R	N	A	X_1	X_2
H	7	88	3	2
OCH_3	2	88	7	3
CH_3	4	83	8	5
F	9	80	5	6
Cl	8	79	5	8
Br	6	80	8	6

N - Nitrones; A - Aldimines; X_1 - Low boiling compounds; X_2 - High boiling compounds (see text);

[a]In the presence of O_2; [b]In N_2 atmosphere; Irr. time - 30 min.; Solvent - Acetonitrile.

Values in parentheses are measured oxidation potentials at glassy carbon electrode in acetonitrile vs Ag with $LiClO_4$ as supporting electrolyte.

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References

1. Kamat, P.V. *Chem. Rev.* **1993**, 93, 267.
2. Linsbigler, A.L.; Lu, G.; Yates, J.T. *Chem. Rev.* **1995**, 95, 735.
3. Fox, M.A.; Dulay, M.T., *Chem. Rev.* **1993**, 93, 341.
4. Somasundaram, N.; Srinivasan, C. *J. Photochem. Photobiol. A: Chem.* **1996**, 99, 67.
5. Somasundaram, N.; Pitchumani, K.; Srinivasan, C. *J. Chem. Soc. Chem. Commun.* **1994**, 1473.
6. Somasundaram, N.; Srinivasan, C. *J. Org. Chem.* **1996**, 61, 2895.
7. Kuwamura, Y.; Iwano, Y.; Shimizu, Y.; Tokai, Y.; Horie, T. *Chem. Lett.* **1994**, 707.
8. Horner, L.; Hoffman, H. *Angew. Chem.* **1956**, 68, 473; Sivasubramanian, S.; Ramamoorthy, V.; Balasubramanian, G, *OPPI BRIEFS*. **1995**, 27, 221.
9. Vogel, A.I. *Text Book of Practical Organic Chemistry*: Longmans, London, **1959**, 629.