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TiO_2 Catalysed Photo-oxidation of Dimethylglyoxime

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The catalysed photo-oxidation of dimethylglyoxime in near UV-TiO_2 system has been studied. The yield of photoproduct increases as the substrate concentration increases up to a certain limit, and the same observation has been observed with the photocatalyst TiO_2, while photocatalyst having more band gap and solvents having high dielectric constant enhance the yield of photoproduct. A probable mechanistic path has been proposed by considering these observations.

INTRODUCTION

The problems of toxicity and degradation of chemical contaminants are very serious from an ecological point of view[1]. Although biodegradation through bacteria is well known[2–4], lot of chemicals have accumulated in nature because of poor and/or slow bactericidal activity. Water pollution caused by hazardous material is becoming a serious problem globally[5]. The contaminants of numerous chemicals from industry, agriculture and domestic use must be eliminated. Since such chemicals are fungicides, herbicides, insecticides, disinfectants, antimicrobiols, nematicides are difficult to decompose by biodegradation through bacteria they accumulate in nature and persist for a long time. Redox reactions induced by electrons [e^-_{CB}] and hole [h^+_{VB}], photogenerated by excitation of semiconductor particles, can potentially be used for several technical applications[6–9]. When hazardous chemicals are irradiated with ultra-violet light the heterogeneous TiO_2 catalyst shows very strong oxidising property in presence of oxygen. One of the most promising photocatalysts is TiO_2, classified as *n*-type semiconductor, which is stable under photo-irradiation even in aqueous medium[10]. Literature reveals that negligible attention has been paid on sensitised photo-oxidation of biologically important compounds, specially possessing $>C=N$ bonds as these offer reactive sites for environmental degradation or biochemical degradation[9]. Since the molecular mechanism of heterogeneous photochemical reaction of these types of compounds is not known, it is therefore planned to investigate the simpler organic compounds possessing $>C=N$ bonds like dimethylglyoxime which can be used as such or as a model system for evaluating the efficiency of photocatalytic reactions. Basic interest has centred recently on mechanistic questions such as the identity, life times and modes of reactions of the dominant photo-oxidising species produced at the TiO_2 solutions by dimethylglyoxime microinterfaces on UV illumination.

EXPERIMENTAL

Dimethylglyoxime, titanium dioxide (Merck), methanol, ethanol, isopropanol and 1-butanol (BDH) were used. Double distilled methanol was used to prepare all the solutions. 0.20 g of dimethylglyoxime was dissolved in methanol (50 mL) in a beaker; 0.200 g photocatalyst TiO_2 was added to this solution. The solution was then irradiated with a UV light (Toshniwal λ-365 nm) kept at a distance of 20 cm from the upper surface of the reaction vessel. The progress of the reaction was checked with the help of TLC at every 2 h interval. After 4 h of irradiation spots were developed by placing the plates in iodine chamber. Two spots one corresponding to the substrate and another corresponding to the photoproduct were obtained. After 6 h, the reaction was stopped, a photoproduct was separated as 2,4-dinitrophenylhydrazine derivative (recrystallised, m.p. 210°C).

Effect of Amount of Substrate: The effect of the amount of substrate on photocatalytic reaction was studied by using variable amounts of substrate. The yield of photoproduct was determined and results are reported in Table-1.

TABLE-1

Solvent (methanol): 50 mL photocatalyst (TiO_2): 0.200 g
time of irradiation: 360 min

Amount of substrate (g)	% Yield of photoproduct
0.050	6.0
0.100	10.0
0.150	17.0
0.200	23.0
0.250	24.0
0.300	25.0

Effect of Polarity of Solvent: The effect of polarity of the solvent on the yield of photoproduct was studied and observations are summarised in Table-2.

TABLE-2

Dimethylglyoxime: 0.200 g photocatalyst (TiO_2): 0.200 g
time of irradiation: 360 min solvent: 50 mL

Solvent	Dielectric constant (D)	% Yield of photoproduct
1-Butanol	17.10	16.0
Isopropanol	18.30	18.0
Ethanol	24.30	21.0
Methanol	32.63	22.0

Effect of Amount of Photocatalyst: Keeping all other factors identical the effect of amount of photocatalyst titanium dioxide has also been observed and results are given in Table-3.

Effect of Nature of Photocatalyst: The effect of the nature of photocatalyst on photocatalytic reaction was studied by using different photocatalysts like titanium dioxide, zinc oxide, stannic oxide, zinc sulphide, etc. The yield of photoproduct was determined in presence of various photocatalysts. The results are summarised in Table-4.

TABLE-3

Dimethylglyoxime: 0.200 g
solvent (methanol): 50 mL
photocatalyst: TiO_2
time of irradiation: 360 min

Amount of TiO_2 (g)	% Yield of photoproduct
0.025	6.0
0.050	7.0
0.100	12.0
0.150	20.0
0.200	23.0
0.250	24.0

TABLE-4

Dimethylglyoxime = 0.200 gm
sovent (methanol) = 50 mL
photocatalyst = 0.200 g
time of irradiation = 360 min

Photocatalyst	Band gap (ev)	% yield of photoproduct
TiO_2	3.1	22.0
ZnO	3.2	30.0
SnO_2	3.5	33.0
ZnS	3.6	35.0

RESULTS AND DISCUSSION

On the basis of physical, chemical and spectral data the photoproduct was characterised as 2,3-butanedion.

Infra-red analysis shows the absorption band at 1718 cm^{-1}, which shows the presence of α-diketonic group in the photoproduct, whereas no absorption band in the region 1690–1640 cm^{-1} confirms the $>C=N$ group absent in the photoproduct.

After completion of photocatalytic reaction the photoproduct was characterised by its usual qualitative tests. Treatment with (i) sodium nitroprusside solution—wine-red colour, (ii) *m*-dinitrobenzene—red colour, (iii) 2,4-dinitrophenylhydrazine—orange ppt (m.p. 210°C) shows the presence of ketonic group in the photoproduct. The other component was confirmed as HNO_2 by usual tests.

The effect of amount of substrate has been studied on this reaction. It has been observed that as the amount of substrate was increased, the yield of the photoproduct was also found to increase. But this increase in the yield was observed only up to a certain limit. In the present investigation the yield of the photoproduct increased up to 0.200 g of the substrate. Further increase in the amount of substrate showed very low increase in the yield of the photoproduct (Table-1). It may be explained on this basis that as the concentration of substrate increases, more substrate molecules are available for photocatalytic reaction, and hence an enhancement in the rate was observed. On the other hand a decrease in the rate of photocatalytic reaction was observed with increasing concentration of substrate, where more substrate molecules are available to hinder the movement of substrate molecules towards the semiconductor surface[11].

The effect of polarity of solvent on the rate of photocatalytic reaction was also observed and for this purpose various solvents of different dielectric constant were used. It was observed that the rate of this reaction increases with the increase in the polarity of the solvent (Table-2). This suggests that some polar species are involved in this photocatalytic reaction as an intermediate.

The effect of increase in the amount of photocatalyst has also been observed: the yield of the photoproduct was also found to increase. However this increase in the yield was observed only up to a certain amount of the photocatalyst. In the present investigation the maximum yield was obtained for 0.200 g of the photocatalyst. Any further increase in the amount of photocatalyst showed no increase in the yield of the photoproduct. It indicates that there is a limiting value of photocatalyst above which the increase in the amount of photocatalyst will not affect the yield appreciably. This observation may be explained on the basis that in the initial stage, even a small addition of photocatalyst will increase the yield of photoproduct as the surface area of photocatalyst increases, but after a certain amount (0.20 g), addition of photocatalyst does not affect the yield of the product because of the fact that at this limiting amount, the surface at the bottom of the reaction vessel becomes completely covered with the photocatalyst. Now, increases in the amount of photocatalyst will only increase the thickness of the layer of photocatalyst already formed at the bottom of the vessel and not the surface area. Hence, the yield of the photoproduct will remain unaffected by the addition of the photocatalyst above a certain limit (Table-3).

The effect of nature of photocatalyst on the yield of photoproduct has been observed. It was observed that when the source of UV light was employed for irradiation, the yield of photoproduct increased with the increase in the band gap of semiconductor. The yield was higher in the presence of ZnS and relatively in the presence of TiO_2. It can be explained on this basis that the semiconductors having higher band gap absorb more efficiently in UV light (Table-4).

On the basis of the above results and discussion the following tentative mechanism has been proposed for the photocatalytic reaction of dimethylglyoxime.

Metal oxide semiconductor TiO_2 behaves as short-circuited electrochemical cells where both cathodic and anodic electron transfers occur on the same particle. Excitation of TiO_2 (semiconductor) leads to the formation of an electron-hole pair.

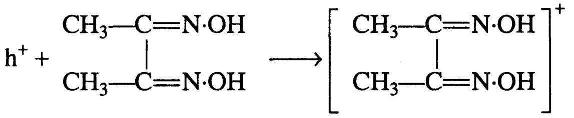
$$TiO_2 \xrightarrow[\text{UV region}]{h\nu} TiO_2^*$$

$$TiO_2^* \longrightarrow e^-_{(CB)} + h^+_{(VB)}$$

Photoexcitation of TiO_2 produces a pair of electron and hole undergoing recombination without any chemical reaction in the absence of any suitable oxidant and/or reductant.

$$e^- + h^+ \longrightarrow TiO_2$$

hole reacts with dimethylglyoxime as follows

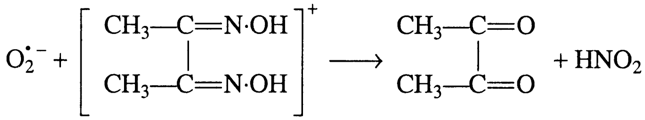


$$h^+ + \begin{array}{l} CH_3-C=N\cdot OH \\ \qquad\;\; | \\ CH_3-C=N\cdot OH \end{array} \longrightarrow \left[\begin{array}{l} CH_3-C=N\cdot OH \\ \qquad\;\; | \\ CH_3-C=N\cdot OH \end{array}\right]^+$$

It has been shown that the presence of oxygen is necessary for photocatalytic oxidation to occur and convert it into oxidising species O_2^- super-oxide.

$$e^- + O_2 \longrightarrow O_2^{\bullet -}$$

Solvent having high dielectric constant enhances the intermediate stage, super-oxide oxidises [dimethylglyoxime]$^+$ into 2,3-butanedione



$$O_2^{\bullet -} + \left[\begin{array}{c} CH_3-C=N\cdot OH \\ | \\ CH_3-C=N\cdot OH \end{array}\right]^+ \longrightarrow \begin{array}{c} CH_3-C=O \\ | \\ CH_3-C=O \end{array} + HNO_2$$

The overall view can be summarised in Figure 1.

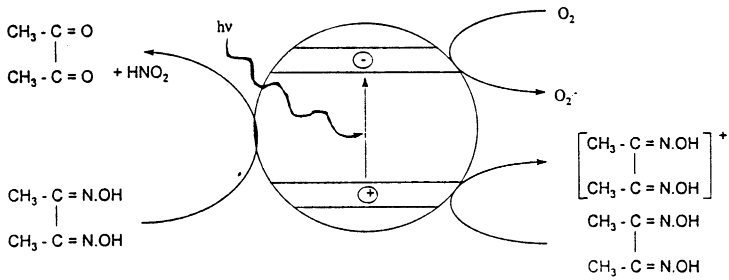


Fig. 1. Schematic illustration of the photocatalytic reaction of dimethylglyoxime

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