Chapter 3

HETEROGENEOUS PHOTOCATALYSED DEGRADATION OF THREE SELECTED ORGANIC POLLUTANTS, MALEIC HYDRAZIDE, BENZIDINE AND 1,2-DIPHENYL HYDRAZINE IN AQUEOUS SUSPENSIONS

3.1 Abstract

The photocatalysed degradation of three selected organic pollutants, namely maleic hydrazide (1), benzidine (2) and 1,2-diphenyl hydrazine (DPH, 3) has been investigated in aqueous suspensions of titanium dioxide (TiO2) under a variety of conditions. The degradation of maleic hydrazide (1) was studied employing UV spectroscopic analysis technique whereas the degradation of benzidine (2) and 1,2-diphenyl hydrazine (3) was studied using HPLC analysis technique. The mineralization of all the compounds under investigation was studied by measuring the decrease in total organic carbon (TOC) content as a function of irradiation time. The degradation kinetics were studied under different conditions such as reaction pH, substrate and photocatalyst concentration, type of TiO2 photocatalyst and the presence of alternative additives such as H2O2 and KBrO3 besides molecular oxygen. The degradation rates and the photonic efficiencies were found to be strongly influenced by the above parameters. The two intermediate products such
as 4-amino-biphenyl (8) and hydroquinone (14) were identified through GC-MS analysis technique in the photocatalytic reaction of benzidine. A probable pathway for the formation of the products has been proposed.

3.2 Introduction

The model compound, maleic hydrazide (1) is used as a herbicide and plant growth inhibitor.\(^1\) It is used for the suppression of grass growth on lawns, roadside verges, amenity areas, and also for the growth of shrubs and trees. It works as a growth retardant by inhibiting the mitotic division in plants thus indirectly killing weed by inhibiting their growth. It’s solubility in water has been reported as 4.5 g L\(^{-1}\).\(^2\) Due to its high solubility it can either penetrates deep into the soil ultimately reaching to the ground water or it can be washed away by rain or irrigation water to the surface water bodies.

The second model compound, benzidine (2) constitutes an important class of organic pollutant, which has been used in the past, in industries in large amounts to produce dyes for cloth, paper, and leather. However, it has not been manufactured for sale in United States since the mid-1970. Major U.S. Dye companies no longer make benzidine-based dyes. Benzidine has been found in at least 27 of the 1,430 National Priorities List sites identified by the Environmental Protection
Agency. In the past, benzidine entered the environment largely during its manufacture, processing, or use to produce dyes. It evaporates slowly, especially from water and soil. Exposure to high levels of benzidine may cause cancer of urinary bladder and other types of cancer. The biodegradation and thermal degradation of benzidine has been reported earlier. The photodegradation of chlorobiphenyl derivatives in the presence of TiO$_2$ has also been reported. To the best of our knowledge no major effort have been made to study the photocatalytic degradation of these compounds in the presence of titanium dioxide. Therefore we have undertaken a detailed investigation of the photodegradation of maleic hydrazide (1) benzidine (2) and 1,2-diphenyl hydrazine (DPH, 3) sensitized by TiO$_2$ in aqueous suspension under a variety of conditions and an attempt have been made to identify the intermediate products formed in the photocatalytic degradation of the model compounds.
Chart 3.1

1. Maleic hydrazide

2. Benzidine

3. Diphenyl hydrazine
3.3 EXPERIMENTAL

3.3.1 Materials

Reagent grade maleic hydrazide (1) benzidine (2) and 1,2-diphenyl hydrazine (3) were obtained from Aldrich and used as such without any further purification. The water employed in this study was either double distilled or purified by a Milli-Q/RO system (Millipore) to make stock solution. The photocatalyst Degussa P25 (Degussa AG), 8 and Hombikat UV100 (Sachtleben chemie GmbH), 9 was used in most of the experiment. Other catalyst powders namely PC500 (Milenium inorganic chemicals), 10 Kat 26 (TCI Transcommerce International AG, Switzerland) 11 and TTP (Travancore titanium products, India) 12 were used for comparative studies. The other chemical used in this study such as NaOH, HNO3, H2O2 and KBrO3 were obtained from Merck.

3.3.2 Procedure

Solutions of desired concentrations of maleic hydrazide (1) were prepared in double distilled water and for irradiation an immersion well photochemical reactor made of Pyrex glass was used. The solution (250 mL) was filled into the reactor and required amount of photocatalyst was added which was stirred for at least 30 minutes in the dark to allow equilibration of the system. The zero time reading was obtained from
blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp.

For studies on benzidine (2) and 1,2-diphenyl hydrazine (DPH, 3), the solutions were prepared in water purified by Millipore system. The irradiations were carried out in a photochemical reactor was made of Duran glass with a plain quartz window (through which the parallel light beam is entering) equipped with a magnetic stirring bar, a water-circulating jacket, and 5 openings for electrodes and gas supplies. For the irradiation aqueous solution of the compound (250 mL) of the desired solution were filled into the reactor and required amount of photocatalyst was added. The solution was stirred for at least 30 minutes in the dark to allow equilibration of the system. To ensure a constant pH-value throughout the experiment, avoiding the addition of any buffer solution a pH-stat technique was employed. Details about this technique were reported elsewhere. To guarantee a constant O₂ concentration the suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a high-pressure mercury lamp (Osram HBO 500W). IR-radiation and short-
wavelength UV-radiation were eliminated by a 10 cm water filter. Samples (10 mL) were collected before and at regular intervals during the irradiation and centrifuged before analysis.

2.3. Actinometry

For compounds such as maleic hydrazide (1) the actinometry measurements was performed using potassium ferrioxalate actinometry. The average light intensity entering the irradiated solution was determined to be $0.28 \times 10^{-6}$ Einstein $l^{-1} s^{-1}$.

For compounds such as benzidine (2) and 1,2-diphenyl hydrazine (3) actinometry was performed using Aberchrome 540 to determine the total incident light intensity within the wavelength region between 310 and 370 nm, which can be absorbed by TiO$_2$. This technique allows the determination of the incident photon flux entering a photoreactor of a specific geometry at the inner front window, thus, avoiding the necessity of corrections for any influences of light reflections taking into account the reactor geometry. The light intensity throughout all experiments in this study was between 100 and 115 mmol photons $l^{-1} \text{min}^{-1}$. 
2.4. Analysis

The degradation of maleic hydrazide (1) was followed by measuring the change in absorption intensity at 303 nm after 75% dilution of the samples using spectroscopic analysis (Shimadzu 1601UV-VIS). The concentrations of benzidine (2) and DPH (3) were measured by HPLC using a Dionex 4500i chromatograph equipped with a reversed phase column Nucleosil 100-10 C18 (Merck). Benzidine and DPH were detected employing an UV-detector at 280 and 290 nm respectively. The eluent for both model compounds consisted of a binary mixture of water and methanol (70: 30 by volume), the flow rate was 1 mL min⁻¹. Concentrations of the substrates were calculated by calibration curves obtained from HPLC-measurements of the respective compound at different concentrations. Total organic carbon (TOC) of 1-3 was measured with a Shimadzu TOC 5000A analyzer by directly injecting the aqueous solutions after centrifugation.

For the characterization of intermediate products from benzidine, aqueous solutions (250 mL) containing TiO₂ (P25, 1 g L⁻¹) were irradiated with a 125 W medium pressure mercury lamp in an immersion well Pyrex glass photoreactor for different time intervals such as 30, 60 and 90 minutes in separate runs. The irradiated mixture
was filtered and extracted with methylene chloride, which was subsequently dried over sodium sulfate. The solvent was removed under reduced pressure to give a residual mixture, which was analyzed by GC-MS. For GC-MS analysis a Shimadzu Gas Chromatograph and Mass Spectrometer (GCMS-QP 5050) equipped with a 25 m CP SIL 19 CB (d= 0.25 mm) capillary column, operating temperature-programmed (50 °C for 10 min and 200 °C for 30 min at the rate of 10 °C m⁻¹) in a splitless mode, injection volume (2.0 μL) with helium as a carrier gas.

3.4 RESULTS

3.4.1 Photolysis of TiO₂ suspensions containing maleic hydrazide (1), benzidine (2) and diphenyl hydrazine (3)

Irradiation of an aqueous suspensions of desired concentrations of 1-3 in the presence of TiO₂ lead to decrease in the concentration and depletion in TOC content as a function of time. As a representative example, Fig. 3.1 shows the change in absorption intensity at 303 nm and depletion in TOC as a function of irradiation time of an aqueous solution of maleic hydrazide (0.5 mM) in the absence and presence of Degussa P25 TiO₂ (1 g L⁻¹) by the "Pyrex" filtered output of a 125 W medium pressure mercury lamp. It was found that no observable loss of the model compound takes place in the absence of photocatalyst.
Figure 3.1: Influence of Photocatalyst on the degradation and mineralization of maleic hydrazide (1) showing the change in absorption intensity at 303 nm and depletion in TOC as a function of time.

Experimental conditions: Maleic hydrazide (0.5 mM), V = 250 mL, Degussa P25 (1 g L⁻¹), 125 W medium pressure Hg lamp, continuous O₂ purging and stirring, t = 2 h.
whereas, 97.12 % decomposition and 83.8 % mineralization of the 1 was observed after 120 min of irradiation. Both the degradation curves can be fitted reasonably well by an exponential decay curve suggesting first order kinetics. The resulting first order rate constant, \( k_1 \), has been used in all subsequent plots to calculate the photonic efficiency ‘\( \zeta \)’ using

\[
\zeta = \frac{k_1 C_0}{I_0} \quad \text{and} \quad \zeta = \frac{k_1 TOC}{I_0}
\]

where, \( C_0 \): initial pollutant concentration, \( TOC \): total organic carbon content, \( k_1 \) apparent first order rate constant and \( I_0 \) is the incident photon flow per unit volume.

3.4.2 Comparison of different Photocatalysts

The photocatalytic degradation of compounds under investigation was studied in the presence of different TiO\(_2\) samples with an aim to find the best catalyst for the degradation of these compounds. Fig. 3.2 shows the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) (0.5 mM) in the presence of different photocatalysts. It was observed that the degradation was slightly faster in the presence of Degussa P25, as compared to the other photocatalysts whereas TTP showed the lowest efficiency. Hence in all following experiments, Degussa P25 was used as the photocatalyst because this
Figure 3.2: Comparison of photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) in the presence of different photocatalysts.

Experimental conditions: Maleic hydrazide (0.5 mM), photocatalysts: P25 (1gL⁻¹), PC500 (1gL⁻¹), UV100 (1gL⁻¹) and TTP (1gL⁻¹), irradiation time = 2 h.
material exhibited the highest overall activity for the degradation of maleic hydrazide (1).

The photonic efficiency for the decomposition and mineralization of benzidine (2) and DPH (3) in the presence of different TiO$_2$ samples is shown in Fig. 3.3 and 3.4 respectively. It is interesting to note that Hombikat UV100 was better for the degradation and mineralization of benzidine (2) whereas PC500 was found to be more efficient in the case of DPH (3)

3.4.3 Influence of pH

The influence of pH on the degradation of maleic hydrazide (1) in aqueous suspensions of TiO$_2$ was studied in the pH range from 3 to 11. Fig. 3.5 shows the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) as a function of reaction pH employing Degussa P25 (1gL$^{-1}$). The photonic efficiency for the decomposition and mineralization of the compound was found to increase with increasing pH from 2 to 9, further increase in pH lead to decrease in the photonic efficiency.

Employing Hombikat UV100 as photocatalyst the degradation and mineralization of benzidine (2) and DPH (3) was studied in aqueous suspensions of TiO$_2$ in the pH range between pH 3 to 9 employing a
Figure 3.3: Photonic efficiencies calculated for the decomposition and mineralization of benzidine (2) in the presence of different photocatalysts.

Experimental conditions: Benzidine (0.5 mM), photocatalysts (1 g L⁻¹), t = 6 h
**Figure 3.4:** Photonic efficiencies calculated for the decomposition and mineralization of DPH (3) in the presence of different photocatalysts. Experimental conditions: DPH (0.5 mM), photocatalysts (1 g L$^{-1}$), t = 6 h
Figure 3.5: Influence of pH on the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1).

Experimental conditions: Maleic hydrazide (0.5 mM), photocatalyst (P25, 1 gL$^{-1}$) reaction pH (2, 4, 7, 9 and 11). irradiation time = 2 h.
pH-stat technique to ensure a constant pH throughout each irradiation. The photonic efficiency for the degradation and TOC depletion of benzidine (2) and DPH (3) as a function of reaction pH in the presence of Hombikat UV 100 is shown in Fig. 3.6 and 3.7, respectively. In both the cases, the highest efficiency for the degradation and TOC depletion is observed at pH 5 as compared to other pH values. The model compounds 1-3 under investigation contain N-H protons and hence they can be protonated and deprotonated under acidic or basic conditions respectively, depending upon their pKa values. At the same time, the lone pair of electrons present at the nitrogen atom is highly delocalised across the benzene ring. Due to low pKa (4.66, 3.57) values of benzidine, the molecule will be present in its protonated form below 3.57 and will be deprotonated above 4.66. It was found that the efficiency for the degradation and for the mineralization of the model compounds, is higher when the molecule is in equilibrium between its protonated and its deprotonated form. Apparently, the photocatalytic oxidation seems to be favored in this structural orientation of the molecule.
Figure 3.6: Influence of pH on the photonic efficiency for the mineralization (TOC) and degradation of benzidine (2).

Experimental conditions: Benzidine (0.5 mM), Hombikat UV 100 (1 g L\(^{-1}\)), pH (3, 5, 7 and 9), t = 6 h
**Figure 3.7**: Influence of pH on the photonic efficiency for the mineralization (TOC) and degradation of DPH (3).

Experimental conditions: DPH (0.5 mM), Hombikat UV 100 (1 g L⁻¹), pH (3, 5, 7 and 9), t = 6 h
### 3.4.4 Influence of Substrate Concentration

The influence of substrate concentration on the degradation rate of compounds 1-3, was studied at different concentrations varying from 0.10 to 1.0 mM. Fig. 3.8 shows the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) as a function of substrate concentration employing Degussa P25 as photocatalyst. It has been observed that the degradation rate (given in terms of photonic efficiency) for the decomposition and mineralization of the compound increases with increasing substrate concentration from 0.25 to 0.5 mM followed by a plateau region at higher pollutant concentrations.

Figure 3.9 and 3.10 shows the photonic efficiency for the degradation and as well as for the mineralization of benzidine (2) and DPH (3) as a function of the substrate concentration employing Hombikat UV 100 as photocatalyst. The efficiency for the degradation and as well as for the mineralization of the compound increases with the increase in the substrate concentration. The results are encouraging from a practical standpoint since there is apparently no inhibition of the photocatalytic mineralization even at higher pollutant concentrations.
Figure 3.8: Influence of substrate concentration on the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1).

Experimental conditions: Substrate concentrations (0.25, 0.5, 0.75 and 1.0 mM), photocatalyst Degussa P25 (1 gL⁻¹), irradiation time = 2 h.
Figure 3.9: Influence of substrate concentration on the photonic efficiency for the mineralization (TOC) and degradation of benzidine (2).

Experimental conditions: Substrate concentration: (0.1, 0.25, 0.5 and 1 mM), Hombikat UV 100 (g L\(^{-1}\)), t = 6 h
Figure 3.10: Influence of substrate concentration on the photonic efficiency for the mineralization (TOC) and degradation of DPH (3).

Experimental conditions: Substrate Concentration: (0.1, 0.2, 0.3 and 0.5 mM), Hombikat UV 100 (g L⁻¹), t = 6 h
3.4.5 Influence of Photocatalyst Concentration

The influence of the photocatalyst concentration on the photonic efficiency for the decomposition and mineralization of compounds 1-3 was investigated using different concentrations of Degussa P25 and Hombikat UV100 varying from 0.5 to 5 gL⁻¹ and the results are shown in Fig. 3.11 - 3.13. It could be seen from the figure that the photonic efficiency for the decomposition for the compounds 1 and 3 improved markedly whereas only slight increase in the efficiency of the mineralization of the compounds was observed when the catalyst concentration was increases from 0.5 to 5 gL⁻¹.

On the other hand, in the case of benzidine (2), the photonic efficiency for the decomposition and mineralization increases with the increase in catalyst concentration from 0.5 to 2 g L⁻¹. A further increase in catalyst loading lead to a slight decrease in the degradation rate as shown in Fig. 3.12.

3.4.6 Influence of Electron Acceptors

The influence of electron acceptors on the photonic efficiency for the decomposition and mineralization of the compounds under investigation has been studied. Figures 3.14 and 3.15 shows the photonic efficiency for the decomposition and mineralization of maleic
Figure 3.11: Influence of catalyst concentration on the photonic efficiency for the decomposition and mineralization of maleic hydrazide (1).

Experimental conditions: Maleic hydrazide (0.5 mM), photocatalyst Degussa P25 concentration (0.5, 1, 2 and 3 g L⁻¹), irradiation time = 2 h.
Figure 3.12: Influence of catalyst concentration on the photonic efficiency for the mineralization (TOC) and degradation of Benzidine (2).

Experimental conditions: Benzidine (0.5 mM), Photocatalyst (Hombikat UV 100), catalyst concentration: (0.5, 1, 2 and 5 g L⁻¹), t = 6 h
Figure 3.13: Influence of catalyst concentration on the photonic efficiency for the mineralization (TOC) and degradation of DPH (3).

Experimental conditions: DPH (0.5 mM), photocatalyst (Hombikat UV 100), catalyst concentration: (0.5, 1, 2 and 5 g L\(^{-1}\)), \(t = 6\) h
Figure 3.14: Photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) in the presence of photocatalyst and varying concentrations of H$_2$O$_2$.

Experimental conditions: Maleic hydrazide (0.5 mM), photocatalyst P25 (1 g L$^{-1}$), H$_2$O$_2$ (0, 1, 3 and 5 mM), irradiation time = 15min.
Figure 3.15: Photonic efficiency for the decomposition and mineralization of maleic hydrazide (1) in the presence of photocatalyst and varying concentrations of KBrO$_3$.

Experimental conditions Maleic hydrazide (0.5 mM), photocatalyst P25 (1 g L$^{-1}$), KBrO$_3$ (0, 1, 3 and 5 mM), irradiation time = 15 min.
hydrazide (1) in the presence of Degussa P25 containing varying concentrations (1-5 mM) of the electron acceptors such as hydrogen peroxide and potassium bromate respectively. It was observed that both bromate ions and hydrogen peroxide influenced the degradation rate at all concentrations investigated. Control experiments were carried out in the presence of these additives without the photocatalyst, where no observable loss of the compound takes place.

The effect of electron acceptors in addition to molecular oxygen on the degradation kinetics of 2 and 3 was investigated as well. It was found that both the model compounds, benzidine (2) and DPH (3) were unstable in the presence of ammonium persulphate as an oxidant, which was indicated by an instant color change, disappearance of the peak in HPLC and also sharp decrease in the TOC content. It was also observed that the addition of an electron acceptor such as hydrogen peroxide in the presence of photocatalyst leads to change in the color of the solution and hence the decrease in the initial concentration of the compound. Only bromate ions are found to enhance the rate for the degradation and for the TOC depletion of benzidine (2) using Degussa P25 as the photocatalyst, as shown by the decrease in concentration and depletion in TOC content as a function of time (Fig. 3.16).
**Figure 3.16:** Comparison for the photocatalytic degradation and for the mineralization (TOC) of Benzidine (2) in the presence of potassium bromate as oxidant.

Experimental conditions: Benzidine (0.5 mM), KBrO₃ (3 mM), P25 (1 g L⁻¹), t = 6 h
3.4.7 Intermediate Products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of 1-3 through GC-MS analysis. We are able to identify two intermediate products from benzidine (2) formed during the photocatalysed degradation. The GC-MS analysis of an irradiated mixture of benzidine for 30 min showed the formation of 4-aminobiphenyl (8) and hydroquinone (14) appearing at retention times, 13.9 and 17.7 min were identified by comparing the molecular ion and mass fragmentation peak with those reported in the GC-MS library. A plausible mechanism for the formation of 8 involving electron transfer reactions and reactions with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 3.1. The model compound 2 upon the transfer of an electron can form the radical cation 4, which may undergo the loss of a proton forming the radical species 6, which upon the addition of a hydroxy radical will give rise to the N-hydroxy compound 5. This intermediate undergoes cleavage followed abstraction of a proton leading to the formation of the observed product (8). The formation of hydroquinone derivative (14), could similarly be understood in terms of the pathways shown in Scheme 3.2. Benzidine upon the transfer of an electron followed by the
Scheme 3.1

\[
\begin{align*}
\text{H}_2\text{N} &- \text{NH}_2  \xrightarrow{\text{h}_0 / \text{TiO}_2}  \text{H}_2\text{N} - \text{NH}_2^+  \\
\text{H}_2\text{N} &- \text{NH}_2 \xrightarrow{\text{OH}^-}  \text{H}_2\text{N} - \text{NH}^+  \\
\text{H}_2\text{N} &- \text{NH}_2 \xrightarrow{\text{- NOH}}  \text{H}_2\text{N} - \text{NH}^+  \\
\text{H}_2\text{N} &- \text{NH}_2 \xrightarrow{\text{+ H}^+}  \text{H}_2\text{N} - \text{NH}_2
\end{align*}
\]
Scheme 3.2

1. \( \text{H}_2\text{N} - \text{NH}_2 \) \( \xrightarrow{\text{hv/ TiO}_2 + \text{e}^-} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

2. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{O}_2} \) \( \text{H}_2\text{N} - \text{CO} \)

3. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{RH (- R')}} \) \( \text{H}_2\text{N} - \text{OH} \)

4. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{h}_2\text{O}_2} \) \( \text{H}_2\text{N} - \text{H}_2\text{O} \)

5. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{CO} \)

6. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

7. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{OH} \)

8. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

9. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{OH} \)

10. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

11. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{OH} \)

12. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

13. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{OH} \)

14. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)

15. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{e}^-} \) \( \text{H}_2\text{N} - \text{OH} \)

16. \( \text{H}_2\text{N} \) \( \xrightarrow{\text{hv/ TiO}_2} \) \( \text{H}_2\text{N} - \text{NH}_2 \)
addition of a hydroxyl radical may lead to the formation of the anionic species 11, which may undergo loss of ammonia followed by the addition a superoxide radical anion to give a peroxy radical species 10. This intermediate on abstraction of a hydrogen atom will give rise to hydroperoxy intermediate 12, which may subsequently lead to the formation of hydroxy compound 13. This on cleavage followed by abstraction of a proton will give the observed product (14) as shown in Scheme 3.2.
References:


8. Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

9. Hombikat UV100 was a gift sample from Schtleben Chemie GmbH, Duisberg, Germany.

10. PC500 gifted by Dr. D. W. Bahnemann from Institut fuer Technische Chemie Universitat Hannover, Callinstrasse, Hannover, Germany.
11. Kat 26 was obtained from TCI Transcommerce International AG, Switzerland.

12. TTP was obtained from Travancore Titanium Products, Trivandrum, India.


16. These experiments were carried out by Dr. M. Muneer at Institut für Solarenergieforschung Hameln/Emmerthal (ISFH), Aussenstelle Hannover, Sokelantstrasse 5, D-30165 Hannover, Germany.