Chapter 3

PHOTOCATALYSED DEGRADATION OF TWO SELECTED TRIPHENYLMETHANE DYE AND A XANTHENE DYE IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE

3.1 Abstract

The photocatalysed degradation of two selected triphenylmethane dyes such as gentian violet (1) and p-rosaniline (2) and a xanthene dye derivative, eosine yellowish (3) have been investigated in aqueous suspension of titanium dioxide under a variety of conditions such as different types of TiO₂, reaction pH, catalyst loading, dye concentration and in the presence of different electron acceptors besides molecular oxygen. The degradation of the dye was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the dye was found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of gentian violet (1) and p-rosaniline (2), whereas Hombikat UV100 was found to be better in the case of eosin yellowish (3). The degradation products were analysed by GC/MS analysis technique and probable pathways for the formation of products have been proposed.

3.2 Introduction

Triphenylmethane and xanthene dye derivatives have also been used extensively in the textile industry and also as a biological stain and paper printing. There are few studies on the degradation of these related systems reported in the literature. For example, Mathews and
coworkers\(^3\) have reported the photocatalytic degradation of rhodamine B using TiO\(_2\) coated sand in a flat bed configuration. The kinetic study on bleaching of rhodamine 6G photosensitized by titanium dioxide has also been reported earlier by Mills and coworkers.\(^4\) The photocatalytic degradation of erythrosine, rhodamine B and eosine using TiO\(_2\) has been reported by Ma et al. and Hidaka and coworkers.\(^5\)–\(^7\) Zhao et al. has reported the photocatalytic degradation of cationic dye, rhodamine B using TiO\(_2\) in the presence of anionic surfactant.\(^8\) The photocatalytic degradation of acid green 16 using ZnO has also been reported under different conditions by Sakthivel et al.\(^9\)

We have studied the degradation of two selected triphenylmethane dyes, gentian violet (1) and p-rosaniline (2) and a xanthene dye derivative eosine yellowish (3) (Chart 3.1) sensitized by TiO\(_2\) in aqueous solution under varying conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

### 3.3 Experimental

#### 3.3.1 Reagent and chemicals

Gentian violet (1) from BDH, Poqle, England, p-rosaniline (2) from Ottoic Kemi India Pvt, Ltd and eosine yellowish (3) from Johnson & Sons Hindan London were obtained and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide samples such as Degussa P25,\(^10\) Hombikat UV100 (Sachtleben
Chart 3.1

1. (Gentian violet)

2. (p-rosaniline)

3. (Eosine Yellowish)
chemie GmbH) and PC500 (Milenium inorganic chemicals) were used for the degradation studies. The other chemical used in this study such as NaOH, HNO₃, (NH₄)₂S₂O₈, H₂O₂ and KBrO₃ were obtained from Merck.

Irradiations were carried out in an immersion well photochemical reaction vessel made of Pyrex glass (Fig. 1.2) using 125 W medium pressure mercury lamp.

3.3.2 Analysis

The degradation of the dye derivatives 1-3 was followed UV Spectroscopically by measuring the decrease in absorption intensity at 536 nm, 518 nm and 544 nm after 80%, 83% and 80% dilution with doubled distilled water as function of irradiation time. The mineralization of the dyes under investigation was monitored by measuring the depletion in TOC as function of irradiation time using Schimadzu 5000 A TOC Analyzer. For the characterization of the degradation product, the aqueous solution of the dye was irradiated in the presence of photocatalyst using 125 W medium pressure mercury lamp. The irradiated mixture was extracted with chloroform after removed the photocatalyst, dried over anhydrous sodium sulphate and the solvent was removal under reduced pressure to give a residual mass, which was analysed by GC/MS analysis technique.

3.4 Results and Discussion

3.4.1 Irradiation of an aqueous solution of the dye in the presence of TiO₂

The aqueous solution of desired concentrations of the dye derivatives, 1-3 in the presence of photocatalyst (TiO₂, 1 gL⁻¹) was irradiated by Pyrex filtered out put of a 125 W medium pressure
mercury lamp under oxygen atmosphere. As a representative example, the change in absorption intensity and depletion in TOC content as function of irradiation time in the presence and absence of the photocatalyst is shown in Fig. 3.1 for the photocatalytic degradation of gentian violet (1). It could be seen from the figure that 85% mineralization and 99% decomposition of the dye takes place in the presence of photocatalyst, whereas no change was observed in the absence of photocatalyst. Both the curves can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics. The degradation rate for the mineralization and decomposition of the dye was calculated in terms of mole L\(^{-1}\) min\(^{-1}\).

The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.4.2 Comparison of different photocatalysts

We have tested the photocatalytic activity of three different commercially available TiO\(_2\) powders (namely Degussa P25, Hombikat UV100, PC500) on the degradation kinetics of 1-3. Fig. 3.2-3.4 shows the degradation rate obtained for the TOC depletion an decomposition of 1-3, in the presence of different types of TiO\(_2\). It has been observed that the degradation of triphenylmethane dyes 1 and 2 proceed much more rapidly in the presence of Degussa P25, whereas the degradation of xanthene dye, 3 is faster in the presence of Hombikat UV100 as compared with other TiO\(_2\) samples. It is interesting to note that the photocatalyst Degussa P25 was found to be more efficient for the degradation of all the compounds studied in Chapter 1 and 2, when irradiated with UV light source. In contrast the photocatalyst Hombikat UV 100 was found to be more effective for the photocatalytic degradation of this particular xanthene dye derivative 3.
Figure 3.1: Depletion in TOC and change in absorption intensity at 536 nm as a function of irradiation time for an aqueous solution of gentian violet (1) in the presence and absence of photocatalyst. Experimental conditions: dye concentration (0.18 mM), V = 250 mL, immersion well photoreactor, 125 W medium pressure Hg lamp, Photocatalyst: Degussa P25 (1 gL⁻¹), absorption intensity was followed at 536 nm after 80% dilution, cont. O₂ purging and stirring, irradiation time=90 min.
Figure 3.2: Comparison of degradation rate for the decomposition and mineralization of gentian violet (1) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.18 mM), V = 250 mL, Photocatalysts: Degussa P25 (1 g L⁻¹), Hombikat UV100 (1 g L⁻¹) and PC500 (1 g L⁻¹), absorption intensity was followed at 536 nm after 80% dilution, irradiation time = 90 min.
Figure 3.3: Comparison of degradation rate for the decomposition and mineralization of p-
rosaniline (2) in the presence of different photocatalysts. Experimental conditions: dye
concentration (0.25 mM), V=250 mL, Photocatalysts; Degussa P25 (1 gL^{-1}), Hombikat UV100 (1
gL^{-1}) and PC500 (1 gL^{-1}), absorption intensity was followed at 544 nm after 80% dilution,
irradiation time=90 min.
Figure 3.4: Comparison of degradation rate for the decomposition and mineralization of eosine yellowish (3) in the presence different photocatalysts. Experimental conditions: dye concentration (0.25 mM), \( V = 250 \text{ mL} \), Photocatalysts: Degussa P25 (1 gL\(^{-1}\)), Hombikat UV100 (1 gL\(^{-1}\)) and PC500 (1 gL\(^{-1}\)), absorption intensity was followed at 518 nm after 83% dilution, irradiation time=30 min.
Although the photocatalyst Degussa P25 is lower in anatase content, specific BET-surface area and primary particle size with that of Hombikat UV100, this photocatalyst has been found to be more efficient for the degradation of majority of organic compounds studied earlier\textsuperscript{15-18} and in this thesis. These results indicate that the efficiency of photocatalyst for the degradation of organic pollutants depends upon the types of chromophore present in the molecule and other reaction parameters.

3.4.3 pH Effect

Employing Degussa P25 and Hombikat UV100 as photocatalyst the degradation rate for the TOC depletion and decomposition of the dye derivatives 1-3 was studied in the pH range between 3 to 11 and the results are shown in Fig. 3.5-3.7. The efficiency of degradation rate for the decomposition of dye 1 was better at pH 3 and 11, whereas it was lower at pH values 5.8 and 9. In contrast, the rate for the mineralization of the dye was found to decrease with the increase in pH from 3 to 9 and a further increase in pH leads to increase in the rate. The degradation rate for the TOC depletion and decomposition of the dye derivative 2 was found to be highest at pH 3.3, which slowly decreases with the increase in pH. Similarly, in the case of 3 highest efficiency was observed at pH 5, which decreases with increase in pH.

The adsorption of dye on the surface of the photocatalyst was investigated by stirring their solution in dark for 24 h in a round-bottomed flask containing varying amounts of Degussa P25 (dye 1 and dye 2) and Hombikat UV100 (dye 3) at different pH values. Analysis of the sample after centrifugation indicate some observable loss of gentian violet (1) at pH 3 and 4.6, whereas no observable loss of the dye was seen in the case of p-rosaniline (2) and eosine yellowish (3) in the
Figure 3.5: Influence of pH on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentration (0.18 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 4, 6, 9 and 11), irradiation time=90 min.
Figure 3.6: Influence of pH on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 5, 7 and 9), irradiation time=90 min.
Figure 3.7: Influence of pH on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 gL⁻¹), reaction pH (5.3, 7, 9, 11), irradiation time=30 min.
pH range studied (3 to 11).

3.4.4 Effect of substrate concentration

The effect of substrate concentration on the degradation of 1-3 has been investigated at varying concentrations of the dye. Fig. 3.8-3.10 shows the degradation rate for the TOC depletion and decomposition of the dye derivatives 1-3 as a function of dye concentration employing Degussa P25 and UV100 as photocatalyst. It has been observed that in the case of 1, the degradation rate increases with the increase in substrate concentration from 0.18 to 0.25 mM and a further increase in the substrate concentration from 0.25 to 0.5 mM leads to slight decrease in the degradation rate of the dye as shown in Fig. 3.8. In the case of dye derivatives 2 and 3 the rate has been found to decrease with the increase in substrate concentration from 0.25 mM to 0.75 mM. The reason for lower rates for the degradation of dyes at higher substrate concentrations has already been discussed in Chapter 1.

3.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of 1-3 were investigated employing different catalyst loading of Degussa P25 in the case of 1 and 2 and UV100 for the dye derivative 3 varying from 0.5 to 5 gL⁻¹. As expected, the degradation rate for the TOC depletion and decomposition of the dye was found to increase with the increase in catalyst concentration as shown in Fig. 3.11, 3.12 and 3.13 respectively.
Figure 3.8: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentrations (0.18, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time= 90 min.
Figure 3.9: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time=90 min.
Figure 3.10: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa UV100 (1 g L⁻¹), irradiation time=30 min.
Figure 3.11: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentration (0.18 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 gL⁻¹), irradiation time=90 min.
Figure 3.12: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental condition: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 g L⁻¹), irradiation time=90 min.
Figure 3.13: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentration (0.25 mM), \( V = 250 \text{ mL} \), Photocatalyst: Hombikat UV100 (0.5, 1, 2 and 5 gL\(^{-1}\)), irradiation time = 30 min.
3.4.6 Effect of electron acceptors

The effect of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate in addition to molecular oxygen on the degradation kinetics of the model compounds 1-3 were investigated as well. It was found that the model compound gentian violet (1), undergoes coagulation in the presence of ammonium persulphate and TiO₂ in the dark, which was indicated by the separation of the dye from the solution. On the other hand, the electron acceptors such as hydrogen peroxide and potassium bromate have been found to enhance the efficiency of degradation as shown by the depletion in TOC as a function of irradiation time (Fig. 3.14). It is interesting to note that when the reaction was carried out in the presence of potassium bromate using Degussa P25, the TOC depletion is very fast at the initial irradiation time, which slowly decreases with increasing irradiation time.

The degradation rate for the decomposition and mineralization of p-rosaniline (2) in the presence of potassium bromate and hydrogen peroxide containing Degussa P25 is shown in Fig. 3.15. The electron acceptor such as potassium bromate has been found to markedly enhanced the degradation rate for the decomposition of the dye as shown in the figure.

The degradation rate for the decomposition and TOC depletion of eosine yellowish (3) in the presence of hydrogen peroxide and ammonium persulphate is shown in Fig. 3.16. Both the additives showed beneficial effect on the degradation rate for the decomposition of the dye whereas the effect of these additives on the TOC depletion is not pronounced.
Figure 3.14: Effect of hydrogen peroxide and potassium bromate on TOC depletion as a function of irradiation time for the photocatalytic degradation of gentian violet (1). Experimental condition: dye concentration (0.18 mM), V=250mL, Photocatalyst: Degussa P25 (1 gL⁻¹), Electron Acceptor: H₂O₂ (10 mM) and KBrO₃ (3mM), irradiation time=90 min.
Figure 3.15: Comparison of degradation rate for the decomposition and mineralization of p-
rosaniline (2) in the presence of different electron acceptors. Experimental condition: dye
congentration (0.25 mM), V=250mL, Photocatalyst: Degussa P25 (1 g·L⁻¹), Electron Acceptors:
KBrO₃ (5 mM), H₂O₂ (10 mM), irradiation time=90 min.
Figure 3.16: Comparison of degradation rate for the decomposition and mineralization of eosine yellowish (3) in the presence of different electron acceptors. Experimental condition: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 gL⁻¹), Electron Acceptors: H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (3 mM), irradiation time=30 min.
3.4.7 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye in aqueous suspension of titanium dioxide through GC/MS analysis technique. The GC/MS analysis of the irradiated mixture of (1, 0.25 mM) for 120 min shows the formation of several degradation products. Out of which two products appearing at retention times (t<sub>r</sub>) 8.45 min and 9.30 min could be assigned to N-methylaniline (10) and p-aminobenzoic acid (16) based on their molecular ion and mass spectrometric fragmentation peaks, as shown below:

**Compound 10:** 107 (M<sup>+</sup>), 104, 83, 73, 71 and 51.

**Compound 16:** 137 (M<sup>+</sup>), 121, 107, 93, 86, 73, 69, 63, 55 and 49.

A plausible mechanism for the formation of these products involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 3.1 and 3.2 respectively.

The model compound 1 upon the transfer of an electron can form to the radical species 4, which may undergo addition of a hydroxyl radical forming 7 which may undergo cleavage either by abstracting a hydroxyl radical to form 6 or by abstracting a proton to form 9 along with the benzophenone derivative 5. The compound 1 on further transfer of an electron can form the radical cation 8, which may subsequently undergo loss of methyl group to give the observed product 10 as shown in Scheme 3.1. The formation of p-aminobenzoic acid (16) could be understood in terms of the pathways shown in Scheme 3.2. The benzophenone derivative 5, upon the transfer of an electron can form the radical anion 11, which can undergo addition of a hydroxyl
Scheme 3.1

1. $\text{H}_3\text{C}^\text{N} \text{CH}_3 \rightarrow \text{hv/TiO}_2 \rightarrow \text{CH}_3^\text{N} \text{CH}_3$

2. $\text{CH}_3^\text{N} \text{CH}_3 \rightarrow \text{OH}^$
Scheme 3.2

5 + hv/TiO₂ → 11

5 + e⁻ → 11

12 + 9 → 13

15 → 16

16 → 15

12 + 9 → 13

14 + 15 → 16
radical forming the anionic species 13, which upon cleavage can lead to the formation of aniline and benzoic acid derivatives 8 and 12 respectively. The compound 12 on further transfer of an electron can give rise to radical cation 14, which may subsequently undergo loss of methyl group to give the observed product 16 as shown in Scheme 3.2.

The irradiated mixture of an aqueous solution of p-rosaniline (2, 0.25 mM) for 1 h showed the formation of several intermediate products through GC/MS analysis technique. Two products 18 and 22 have been proposed based on their molecular ion and mass spectrometric fragmentation peaks as indicated below;

**Compound 18**: 212 (M⁺), 202, 191, 177, 167, 155, 139, 128, 112, 99, 91, 84, 67 and 57.

**Compound 22**: 182 (M⁺), 177, 167, 153, 149, 131, 121, 115, 104, 96, 87, 69, 62 and 55.

The formation of 18 and 22 from the dye derivative 2 could be understood in terms of pathways shown in Scheme 3.3.

The model compound 2 upon the transfer of an electron can form to the radical species 17, which may undergo addition of a hydroxyl radical to give 19. The abstraction of hydroxyl hydrogen either by superoxide radical anion or by hydroxyl radical followed by loss of an aniline moiety may lead to the formation of the observed product 4,4'-diaminobenzophenone (18). The formation of 22 could similarly be understood in terms of the pathways shown in Scheme 3.3. The compound 18 upon the transfer of an electron can lead to the radical cation 20, which may undergo loss of NH₃ to give the product 21, which may in turn undergo similar subsequent reaction leading to the formation of the observed product benzophenone (22).
The GC/MS analysis of an irradiated mixture of eosine yellowish (3, 0.25 mM) for 1 h indicate the formation of several intermediate products as shown in Fig. 3.17. The molecular ion and mass spectrometric peaks of these intermediate products did not give any conclusive evidence for the identification of any product.
Figure 3.17: GC/MS spectra of an irradiated mixture of eosine yellowish (3) in aqueous suspension of titanium dioxide.
References:


10. The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

11. The photocatalyst Hombikat UV100 was a gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fuir Technische Chemie, Universitat, Callinstrasse, Hannover, Germany.
12. The photocatalyst PC500 gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fuir Technische Chemie, Universitat, Callinstrasse, Hannover, Germany.

13. Total Organic Carbon Analyzer was gift equipment from The Alexander von Humboldt-Stiftung, Bonn, Germany.

14. GC/MS analysis was carried out from The Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India.


