Chapter 2

HETEROGENEOUS PHOTOCATALYSED DEGRADATION OF URACIL AND ITS BROMODERIVATIVES IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE

2.1 Abstract

The photocatalysed degradation of uracil (1) and its bromoderivatives such as 5-bromouracil (2) and 5-bromo-3-secondarybutyl-6-methyl uracil (bromacil, 3), has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the compound under investigation was studied using various parameters such as, different types of TiO$_2$ powders, pH, catalyst and substrate concentrations, and in the presence of electron acceptors like hydrogen peroxide (H$_2$O$_2$) and potassium bromate (KBrO$_3$) besides molecular oxygen. TiO$_2$ sample, Degussa P25 was found to be more efficient for the degradation of all the compounds under study. An attempt was made to identify the intermediate products formed during the photooxidation process of the compounds 1-3 in aqueous suspensions of TiO$_2$ through GC-MS analysis technique. The
GC-MS analysis of an irradiated mixture of bromacil (3) lead to the formation of 5-hydroxy-3-sec.butyl-6-methyl uracil (4) and diisopropyl urea (18). A probable pathway for the formation of these products has been proposed.

2.2 Introduction

An another class of compound that is extensively used as herbicide is a uracil derivative. Uracil (1), a pyrimidine base, may be utilized preferentially for nucleic acid biosynthesis in tumors.\(^1\) Substitution at 5-position of uracil by halogen atom results in the drastic changes in the biological properties of the compound.\(^2\) Bromacil (3) is used as a preemergent herbicide. It is used as a selective herbicide to control annual and perennial grasses, broad leaf weeds and woody and plants at non-cropland area.\(^3\) It is used at the rates of 2 to 4 kg per hectare.\(^4\) It is a highly persistent herbicide with an average half life of 5-6 months and in soil it may remain active for about 7 months. It has been found in the ground water of Florida.\(^5\) Earlier studies\(^6,7\) have demonstrated a poor biodegradability of the pesticide derivative such as bromacil.

Few studies related to the degradation of uracil (1) and its bromoderivatives have been reported earlier. Aliskandarani et. al.\(^8\) has
studied the influence of pollutant concentration, volume of solution and stirring speed on the photodegradation of uracil (1) and 5-halouracils in the presence of titanium dioxide. Vaz. et. al.⁹ has studied the influence of pH and anion on the photomineralization of these systems.

The photodegradation of water samples taken from a heavily polluted well containing various types of herbicides have been reported by Muszkat et. al.¹⁰ A study of TiO₂ mediated phototcatalytic degradation of bromacil in the presence of methylene blue has also been reported by Muszkat et. al.¹¹ Degradation of bromacil using chemical oxidation process such as ozonolysis has also been reported earlier.¹²

Inspite of these studies, no major efforts have been made to study the details of the degradation kinetics, the knowledge of which is essential for the proper design of the treatment plant. Therefore we have undertaken the detailed kinetic study of uracil (1), 5-bromouracil (2) and bromacil (3) under different parameters. An attempt has also been made to identify the intermediate products formed in the photocatalytic degradation of compounds 1-3 as shown in Chart 2.1.
Chart 2.1

1. Uracil

2. 5-bromouracil

3. Bromacil
2.3 Experimental

2.3.1 Reagents and chemicals

Reagent grade uracil (1) and 5-bromouracil (2) and analytical grade bromacil (3) were used as such without any further purification for the degradation study. The photocatalyst, titanium dioxide Degussa P25 (Degussa AG), was used in most of the experiment, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH), PC500 (Millennium inorganic chemicals) and TTP (Travancore titanium products, India) were used for comparative studies. The other chemical used in this study such as NaOH, HNO₃, H₂O₂ and KBrO₃ were obtained from Merck. Irradiations were carried out in an immersion well photochemical reaction vessel made of pyrex glass using 125W medium pressure mercury lamp.

2.3.2 Analysis

The degradation of uracil (1) and 5-bromouracil (2), was followed by measuring the decrease in absorption intensity at 259.5 and 277 nm respectively as a function of irradiation time after 75-80% dilution. The mineralization of uracil (1) and its bromoderivatives, 2 and 3 was monitored by measuring the depletion in TOC as a function of irradiation time using Shimadzu 5000A TOC Analyzer.
2.3.3 Characterization of intermediate photoproducts

For characterization of the intermediate products, aqueous solutions (250mL) of the compound containing TiO$_2$ (P25, 1gL$^{-1}$) were taken in a photochemical reactor made of Duran glass with a plain quartz window (through which a parallel light beam is entering) equipped with a magnetic stirring bar, a water circulating jacket and opening for gas supplies. Irradiations were carried out using a high-pressure mercury lamp (Osram HBO 500 W). IR-radiation and short wavelength UV-irradiation were eliminated by a 10 cm water filter. A 320-nm cut-off filter was used to avoid any direct excitation of the compound under investigation. Samples were collected at different time intervals during the irradiation, centrifuged and extracted with methylene chloride, which was subsequently dried over anhydrous sodium sulphate and analyzed by GC-MS. For GC-MS analysis a Shimadzu Gas chromatograph and mass spectrometer (GCMS-QP 5050) equipped with a 25m CP SIL 19 CB (d =0.25mm) capillary column, operating temperature programmed (220°C for 40 min at the rate of 10°C min$^{-1}$) in splitless mode injection volume (1.0 µL) with helium as a carrier gas was used.
2.4 Results and Discussion

2.4.1 Irradiation of an aqueous suspension of uracil (1) and its bromoderivatives (2 and 3) containing TiO$_2$

Irradiation of an aqueous solution of uracil (1) and its bromoderivatives (2 and 3) in the presence of the photocatalyst (TiO$_2$, Degussa P25, 1gL$^{-1}$) by the pyrex filtered output of a 125 W medium pressure mercury lamp under oxygen lead to the decrease in the absorption intensity and depletion in TOC content as a function of time. Fig. 2.1 and 2.2 shows the change in the absorption intensity and depletion in TOC as a function of irradiation time for the photocatalytic degradation of uracil (1) and 5-bromouracil (2). Fig. 2.3 shows the depletion in TOC as a function of irradiation time for the degradation of bromacil (3). Control experiments were carried out in the absence of photocatalyst where there was no observable loss of compound takes place as shown in Fig. 2.1-2.3. Both the curves can be fitted reasonably well by an exponential decay curves suggesting the first order kinetics. The degradation rates for the mineralization of 1-3 and decomposition of 1 and 2 were calculated in terms of M min$^{-1}$. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.
Figure 2.1: Depletion in TOC and change in absorption intensity at 259.5 nm as a function of irradiation time for the photocatalysed degradation of uracil (1) in the presence and absence of TiO$_2$ in the aqueous suspensions.

Experimental conditions: Uracil (0.5 mM), V= 250 mL, 125 W medium pressure Hg lamp, photocatalyst: TiO$_2$ Degussa P25 (1gL$^{-1}$), continuous O$_2$ purging and stirring, irradiation time = 120 min.
**Figure 2.2:** Depletion in TOC and change in absorption intensity at 277 nm as a function of irradiation time for the photocatalysed degradation of 5-bromouracil (2) in the presence and absence of TiO$_2$ in aqueous suspensions.

Experimental conditions: 5-bromouracil (1.0 mM), photocatalyst: TiO$_2$ Degussa P25 (1gL$^{-1}$), irradiation time = 240 min.
Figure 2.3: Depletion in TOC as a function of irradiation time for the photocatalysed degradation of bromacil (3) in the presence and absence of TiO$_2$ in aqueous suspensions.

Experimental conditions: Bromacil (0.48 mM), photocatalyst: TiO$_2$ Degussa P25 (1gL$^{-1}$), irradiation time = 240 min.
The degradation rate for the decomposition and mineralization of the pollutants were calculated using the expressions given below,

\[-d[A]/dt = kc^n \quad [1]\]
\[-d[TOC]/dt = kc^n \quad [2]\]

where,  
k = rate constant,

c = concentration of the pollutant,

n = order of reaction

2.4.2 Comparison of different photocatalysts

The photodegradation of uracil (1) and its bromoderivatives (2 and 3) was tested with four different TiO$_2$ powders, namely, Degussa P25, Hombikat UV100, PC500 and TTP. The degradation rate for the decomposition and mineralization of uracil (1) and 5-bromouracil (2) is shown in Fig. 2.4 and 2.5 respectively whereas Fig. 2.6 shows the degradation rate for the mineralization of bromacil (3).

It could be seen from the figure that in the case of uracil (1), the degradation rate for the decomposition of the compound is much higher in the presence of Degussa P25 as compared with other TiO$_2$ powders. Whereas in the case of 5-bromouracil (2) the influence of Degussa P25
Figure 2.4: Comparison of degradation rate for the decomposition and mineralization of uracil (1) in the presence of different photocatalysts, Experimental conditions: Uracil (0.5 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), Hombikat UV100 (1 gL$^{-1}$), PC500 (1 gL$^{-1}$), irradiation time = 120 min.
Figure 2.5: Comparison of degradation rate for the decomposition and mineralization of 5-bromouracil (2) in the presence of different photocatalysts.

Experimental conditions: 5-bromouracil (1.0 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), Hombikat UV100 (1 gL$^{-1}$), PC500 (1 gL$^{-1}$), irradiation time = 240 min.
Figure 2.6: Comparison of degradation rate for the mineralization of bromacil (3) in the presence of different photocatalysts.

Experimental conditions: Bromacil (0.48 mM), photocatalyst: TiO$_2$ Degussa P25 (1 g L$^{-1}$), Hombikat UV100 (1 g L$^{-1}$), PC500 (1 g L$^{-1}$), irradiation time = 240 min.
on the degradation rate for the decomposition of the compound was not as pronounced as observed in case of 1. In contrast it is interesting to note that in the case of 2 and 3 the degradation rate for the mineralization of the compounds employing photocatalyst Degussa P25 and UV100 is more or less same. The photocatalyst obtained from TTP was found to be of lower efficiency for the degradation of all the compounds under investigation. The reason for the better photocatalytic activity of Degussa P25 has already been discussed in chapter 1. Degussa P25 was used as the photocatalyst for all the remaining experiments since this material exhibited the highest overall activity for the degradation of the model compound under investigation.

2.4.3 Effect of pH

An important parameter in the heterogenous photocatalysis is the reaction pH, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutant and also the size of aggregates it forms. The degradation rate for the decomposition and mineralization of uracil (1) and its bromoderivatives (2 and 3) has been investigated in the pH range between 3 to 9 in the presence of TiO₂.
The degradation rate for the decomposition and mineralization of uracil (1) and 5-bromouracil (2) as a function of reaction pH is shown in Fig. 2.7 and 2.8 respectively. It is interesting to note that the degradation rate for the decomposition of the compounds increases significantly with the increase in the reaction pH whereas its influence on the mineralization rate was not much pronounced. Similar results of the effect of reaction pH on the degradation of uracil (1) and 5-halouracil derivatives have been reported earlier by Vaz et al. 9

Fig. 2.9 shows the degradation rate for the mineralization of bromacil (3) as a function of reaction pH in the presence of three commercially available TiO₂ powders namely Degussa P25, Hombikat UV100, PC500. It could be seen from the figure that the degradation rate for the mineralization of the compound increases with the increase in pH. Interestingly highest rate was observed at pH 9 when photocatalyst Degussa P25 was used.

2.4.4 Influence of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the initial substrate concentration. Hence the effect of initial substrate
Figure 2.7: Comparison of degradation rate for the decomposition and mineralization of uracil (1) at different pH.

Experimental conditions: Uracil (0.5 mM), photocatalyst: TiO₂ Degussa P25 (1 gL⁻¹), reaction pH (3, 5, 7 and 9), irradiation time = 120 min.
Figure 2.8: Comparison of degradation rate for the decomposition and mineralization of 5-bromouracil (2) at different pH.

Experimental conditions: 5-bromouracil (1.0 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), reaction pH (3, 5, 7 and 9), irradiation time = 240 min.
Figure 2.9: Comparison of degradation rate for the mineralization of bromacil (3) at different pH in different photocatalyst.

Experimental conditions: Bromacil (0.48 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), Hombikat UV100 (1 gL$^{-1}$), PC500 (1 gL$^{-1}$), reaction pH (3, 5, 7 and 9), irradiation time = 240 min.
concentration on the degradation of compounds 1-3 was studied at different initial substrate concentrations in the range between 0.12 to 1.5 mM. Fig. 2.10 and 2.11 shows the degradation rate for the decomposition and mineralization of uracil (1) and 5-bromouracil (2) as a function of substrate concentration whereas Fig. 2.12 shows the degradation rate for the mineralization of bromacil (3). The degradation rates of uracil (1) and its bromoderivatives (2 and 3) were found to increase with the increase in the initial substrate concentrations. Interestingly the rate for the decomposition of the compound was found to increase markedly with the increase in substrate concentration in the case of uracil (1).

2.4.5 Effect of catalyst concentration

As the initial reaction rates are directly proportional to the photocatalyst particle or mass. Therefore the influence of the photocatalyst concentrations on the degradation rates was investigated in the range between 0.25 to 5 g L\(^{-1}\). Degradation rate for the decomposition and mineralization of uracil (1) and 5-bromouracil (2) is shown in Fig. 2.13 and 2.14 whereas Fig. 2.15 shows the degradation rate for the mineralization of bromacil (3) in the presence of different concentrations of Degussa P25 photocatalyst. As expected, the rates
Figure 2.10: Degradation rate for the decomposition and mineralization of uracil (1) at different substrate concentration.

Experimental conditions: Photocatalyst: TiO$_2$ Degussa P25 (1 g L$^{-1}$), substrate concentration (0.25, 0.5, 0.75 and 1.0 mM), irradiation time = 120 min.
Figure 2.11: Degradation rate for the decomposition and mineralization of 5-bromouracil (2) at different substrate concentration.

Experimental conditions: Photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), substrate concentration (0.5, 0.75, 1.0 and 1.5 mM), irradiation time = 240 min.
Figure 2.12: Degradation rate for the mineralization of bromacil (3) at different substrate concentration.

Experimental conditions: Photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), substrate concentration (0.12, 0.24, 0.48 and 0.96 mM), irradiation time = 240 min.
Figure 2.13: Degradation rate for the decomposition and mineralization of uracil (1) at different catalyst concentrations.

Experimental conditions: Uracil (0.5 mM), photocatalyst: TiO₂ Degussa P25, catalyst concentrations (0.25, 0.50, 1.0 and 2.0 gL⁻¹), irradiation time = 120 min.
Figure 2.14: Degradation rate for the decomposition and mineralization of 5-bromouracil (2) at different catalyst concentrations.

Experimental conditions: 5-bromouracil (1.0 mM), photocatalyst: TiO$_2$ Degussa P25, catalyst concentrations (0.5, 1.0, 2.0 and 3.0 gL$^{-1}$), irradiation time = 240 min.
**Figure 2.15**: Degradation rate for the mineralization of bromacil (3) at different catalyst concentrations.

Experimental conditions: Bromacil (0.48 mM), photocatalyst: TiO$_2$ Degussa P25, catalyst concentrations (0.5, 1.0, 2.0 and 5.0 gL$^{-1}$), irradiation time = 240 min.
were found to enhance with the increase in concentration of the photocatalyst.

2.4.6 Effect of electron acceptors

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, electron acceptors such as hydrogen peroxide and potassium bromate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the electron/hole \((e^-/h^+\)) pair recombination. Therefore the effect of electron acceptors such as hydrogen peroxide and potassium bromate on the photocatalytic degradation of compounds 1-3 was investigated. Fig 2.16 and 2.17 shows the degradation rate for the decomposition and mineralization of uracil (1) in the presence of different concentrations of hydrogen peroxide and potassium bromate. The degradation rate for the decomposition and mineralization of 5-bromouracil (2) is shown in Fig. 2.18 whereas Fig. 2.19 shows the degradation rate for the mineralization of bromacil (3) in the presence of hydrogen peroxide and potassium bromate. As expected all the additives showed beneficial effect on the degradation rate of the compounds under investigation. It was also observed that bromate ions markedly enhanced the degradation rate of compounds 1-3, while in the presence of hydrogen peroxide a slight
Figure 2.16: Degradation rate for the degradation and mineralization of uracil (1) at different H$_2$O$_2$ concentrations.

Experimental conditions: Uracil (0.5 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), H$_2$O$_2$ concentrations (1, 3, 5 mM), irradiation time = 120 min.
Figure 2.17: Degradation rate for the degradation and mineralization of uracil (1) at different KBrO₃ concentrations.

Experimental conditions: Uracl (0.5 mM), photocatalyst: TiO₂ Degussa P25 (1 gL⁻¹), KBrO₃ concentrations (1, 3, 5 mM), irradiation time = 120 min.
Figure 2.18: Degradation rate for the degradation and mineralization of 5-bromouracil (2) in the presence of electron acceptors.

Experimental conditions: 5-bromouracil (1.0 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), H$_2$O$_2$ and KBrO$_3$ concentrations (3 mM), irradiation time = 240 min.
Figure 2.19: Degradation rate for the mineralization of bromacil (3) in the presence of electron acceptors.

Experimental conditions: Bromacil (0.48 mM), photocatalyst: TiO$_2$ Degussa P25 (1 gL$^{-1}$), H$_2$O$_2$ (10 mM) and KBrO$_3$ (3 mM), irradiation time = 240 min.
increase as compared to the potassium bromate in the degradation rate was observed.

### 2.4.7 Intermediate products

An attempt was made to identify the intermediate products formed during the photoxidation of the compounds 1-3 through GC-MS analysis.

An aqueous suspension of bromacil (0.5 mM, 250mL) in the presence of Degussa P25 (1 gL⁻¹) was irradiated for different time intervals. The catalyst was removed by filtration and the filtrate was extracted with methylene chloride, which was dried over anhydrous sodium sulfate. The removal of the solvent under reduced pressure gave a residual mass which was analysed by GC-MS analysis. The GC-MS analysis showed several products of which two products, 5-hydroxy-3-sec.butyl-6-methyl uracil (4) and diisopropyl urea (18) appearing at retention times (tR) 9.48 and 15.293 min respectively were identified. The photoproduct (4) was identified based on their molecular ion and mass spectrometric fragmentation peaks, whereas the product (18) was identified by comparing the molecular ion and mass fragmentation peaks with those reported in the GC-MS library, which are indicated below;
Compound 4: m/z, 198 (M⁺), 141, 113, 99, 71 and 57.

Compound 18: m/z, 144 (M⁺), 129, 84, 70, 58, 44 and 41.

The formation of 4 and 18 involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system could be understood in terms of the pathways shown in Schemes 2.1 and 2.2 respectively. The model compound 3 upon the addition of a hydroxyl radical followed by loss of bromine radical can lead to the formation of the observed product 4. The compound 4 upon the transfer of an electron can form to the radical cation 6, which may undergo loss of hydrogen atom followed by methyl cation forming 7. This compound on further transfer of electron followed by loss of isopropyl cation may subsequently lead to the formation of 11. Further transfer of an electron from irradiated TiO₂ to the species 8 may lead to the formation of radical anion species 12, which may undergo addition of a hydroxyl radical followed by ring cleavage to give 13 (Scheme 2.2). This compound on subsequent transfer of an electron may undergo addition of hydroxyl radical, ring cleavage and abstraction of isopropyl cation ultimately leading to the formation of the observed diisopropyl urea (18).
Scheme 2.1

3 \rightarrow \text{h} \nu / \text{TiO}_2 + \text{OH}^* \rightarrow 4

5 \rightarrow -\text{H}^* \rightarrow 6

7 \rightarrow -\text{CH}_3 \rightarrow 8

\text{RH (R')} \rightarrow 11
Scheme 2.2

\[
\begin{array}{c}
\text{H}_3\text{C} - \text{N} - \text{CH}_2 - \text{CH}_3 \\
\text{HO} - \text{CO}_2\text{H} \\
\text{8} \\
\text{hv/} \text{TiO}_2 + \text{e}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO}_2 - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{12} \\
\text{OH}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO} - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{14} \\
\text{hv/} \text{TiO}_2 + \text{e}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO}_2 - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{15} \\
\text{OH}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO}_2 - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{16} \\
\text{hv/} \text{TiO}_2 + \text{e}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO}_2 - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{17} \\
\text{OH}^- \\
\text{H}_3\text{C} - \text{N} - \text{CH} - \text{CH}_3 \\
\text{HO}_2 - \text{C} - \text{O} - \text{CO}_2\text{H} \\
\text{18}
\end{array}
\]
References:


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

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

15. PC500 gifted by Dr. D. W. Bahnemann from Institut fuer Technische Chemie Universitat Hannover, Callinstrasse, Hannover, Germany.

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

17. TOC (Total Organic Carbon) analyzer was a gift equipment from Alexander von Humboldt Foundation, Germany.

18. GC-MS spectra was analysed by Dr. M. Muneer at Institut fuer Technische Chemie Universitat Hannover, Germany.