Photochemical reactions of a few selected pesticide derivatives and other priority organic pollutants in aqueous suspensions of titanium dioxide

M. Abu Tariq [b], M. Faisal [b], M. Muneer [a,b,1], D. Bahnemann [c,*]

[a] *Marie Curie Incoming International Fellow, Centre for Material Science, Faculty of Science, University of Central Lancashire, Preston PR1 2HE, UK*
[b] *Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India*
[c] *Institut für Technische Chemie, Gottfried Wilhelm Leibniz Universitaet Hannover, Callinstr. 3, D-30167 Hannover, Germany*

Abstract

In an attempt to improve our understanding of the basic mechanisms of the degradation of aromatic pollutants, the photocatalysed reactions of a few selected organic compounds, namely 4-bromoaniline, 3-nitroaniline, pentachlorophenol, 1,2,3-trichlorobenzene and diphenylamine has been investigated either in water or in acetonitrile/water mixture in the presence of titanium dioxide and molecular oxygen. An attempt has been made to identify the products formed during the photo-oxidation process through GC–MS analysis technique. A probable mechanism for the formation of the products has been proposed.
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1. Introduction

The photocatalysed reaction of organic molecules in the presence of semiconductor such as TiO_2 has become a subject of serious study as it shows promise of a viable commercial technology for the wastewater treatment [1–7]. Among all explorations for potential application, the most active area of the past decade has been the photocatalysis for environmental remediation due to the emerging concern for the environment and the successful destruction of a wide range of pollutants on illuminated semiconductor particles such as TiO_2 [8].

Generally, semiconductor-mediated photocatalysis involves photoexcitaion that causes charge separation in semiconductor particles followed by simultaneous oxidation and reduction of the adsorbed organic substrates. The lifetime of charge separation, the availability of separated charges to the substrate and the thermodynamics of electron transfer reactions determine the efficiency of a redox reaction. Of the two possible pathways for the initial oxidation reactions namely, the one involving direct oxidation of organic substrate and other proceeding through OH$^\bullet$ radical mediated reactions, the current prevailing view favors the latter [9]. However, it is also possible that the nature of the primary process may vary with the nature of the molecule. Organic molecules, which can adhere strongly to the surface of the semiconductors, for example, will be more susceptible to direct oxidation.

The adsorption properties of an organic substrate and its subsequent reactive intermediates and products on the semiconductor surface are also key issues for a synthetically useful redox transformation or degradation. The potential applications of semiconductor-catalysed organic functional group transformations for organic synthesis have also been actively explored [10–12].

It may be used as an alternative method for selective organic synthesis under environmentally benign conditions and achieve the pollution reduction by eliminating potential wastes at their source. Such heterogeneous photocatalysis has been carried out both in organic solvents (usually acetonitrile) [13–20], in aqueous suspensions [21–28] and also in acetonitrile/water mixture [29].

Few studies relating to the degradation of pentachlorophenol [30–35] have been reported earlier. To the best of our

* Corresponding author. Tel.: +49 511 762 5560; fax: +49 511 762 2774.
 E-mail addresses: cht12mm@amu.ac.in, readermuneer@yahoo.co.in
(M. Muneer), bahnemann@iftc.uni-hannover.de (D. Bahnemann).
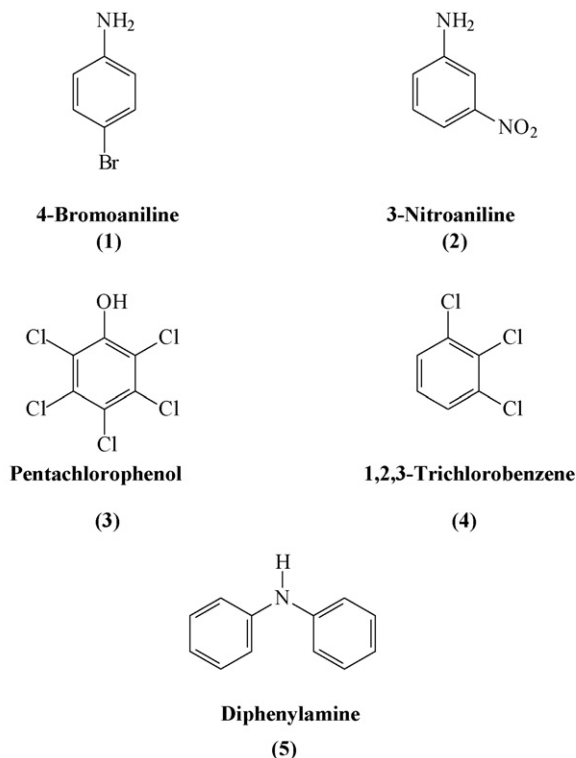 [1] Tel.: +91 571 2703515; fax: +91 571 2702758.
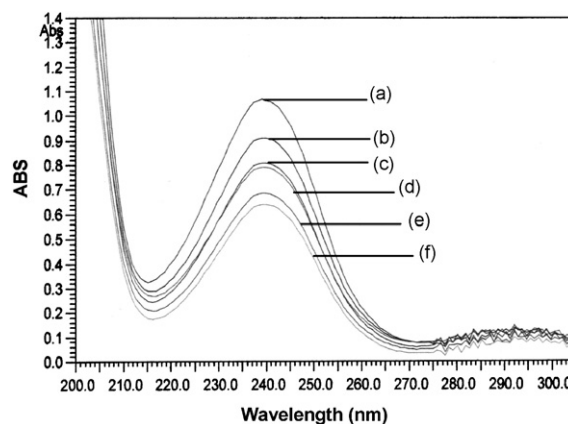
Chart 1. Chemical Structure and Chemical name.

Fig. 1. Change in absorption spectrum of an irradiated mixture of 4-bromoaniline (**1**) in aqueous suspension of titanium dioxide at different time intervals: (a) 0 min; (b)15 min; (c) 30 min; (d) 60 min; (e) 90 min; (f) 120 min.

knowledge no major efforts have been made to look into the photocatalytic degradation of compounds such as bromoaniline and nitroaniline, 1,2,3-trichlorobenzene and diphenylamine (shown in Chart 1). We, therefore, chose to study the photocatalysed reaction of 4-bromoaniline (**1**), 3-nitroaniline (**2**), pentachlorophenol (**3**), 1,2,3-trichlorobenzene (**4**) and diphenylamine (**5**) with the aim of identifying the intermediate products formed during the photo-oxidation process.

2. Experimental

2.1. Reagents

Reagent grade starting materials were obtained from Sigma–Aldrich, Otto-kemi and Loba-chemie and used as such for irradiation experiments. Reagent grade distilled acetonitrile and double distilled water were employed to make solutions of compounds for irradiation experiments. Titanium dioxide (Degussa P25) was used as photocatalyst in this study. Degussa P25 consists of 75% anatase and 25% rutile with a specific BET-surface area of $50 \, m^2 \, g^{-1}$ and a primary particle size of 20 nm [36,37]. Earlier studies [38] indicates that when we do the reaction with Degussa P25 (mixture of anatase and rutile) and with Hombikat UV100 (pure anatase) it led to similar products with some variation in the yields of distribution of products.

2.2. Procedure

The desired concentration of the compound was prepared either in water or in acetonitrile/water mixture and taken in

an immersion well photochemical reaction vessel made of Pyrex glass (150 mL capacity), to avoid the direct excitation of the molecule (a case of sensitized irradiation). The required amount of photocatalyst TiO_2 (Degussa P25) was added and irradiated using 125 W medium-pressure mercury lamp (radiant flux $\approx 4890 \, \mu W/cm^{-2}$) with continuous stirring and purging with molecular oxygen. It could be seen from Fig. 1 that the absorption intensity decreased with increasing irradiation time. The photonic efficiencies of all the reactions were found to be in the range of 50–70% at their respective irradiation time. The irradiated mixture was filtered and extracted with chloroform, which was subsequently dried over anhydrous sodium sulfate. The removal of the solvent under reduced pressure gave a residual mass, which was analyzed by GC/MS. For GC/MS analysis a Schimadzu gas chromatograph and mass spectrometer (GCMS-QP 5000) equipped with a 25 m CP SIL 19 CB ($d = 0.25$ mm) capillary column, temperature programmed (injection temp., column temp., 260 °C for 25 min at the rate of 10 °C min^{-1} in a split mode, injection volume 1.0 μL) was used with helium as a carrier gas.

3. Results and discussion

3.1. Photocatalysis of TiO_2 suspensions containing 4-bromoaniline (**1**)

A solution of 4-bromoaniline (**1**, 2 mM) in water was irradiated with a 125 W medium-pressure mercury lamp in presence of TiO_2 (Degussa P25, 1 g L^{-1}) for 2 h under oxygen atmosphere. The catalyst was removed and the irradiated mixture was extracted with chloroform which was dried over anhydrous sodium sulfate and removed under reduced pressure to give a residual mass. The GC–MS analysis of the residue, reveal the formation of several products as shown in Fig. 2a and b, of which three products, namely 4-bromophenol (**7**), 1-bromo-4-nitrobenzene (**11**) and 4,4′-dibromoazobenzene (**13**) appearing at retention times (t_R) 5.6, 6.0 and 13.3 min, respectively, were identified by comparing the molecular ion
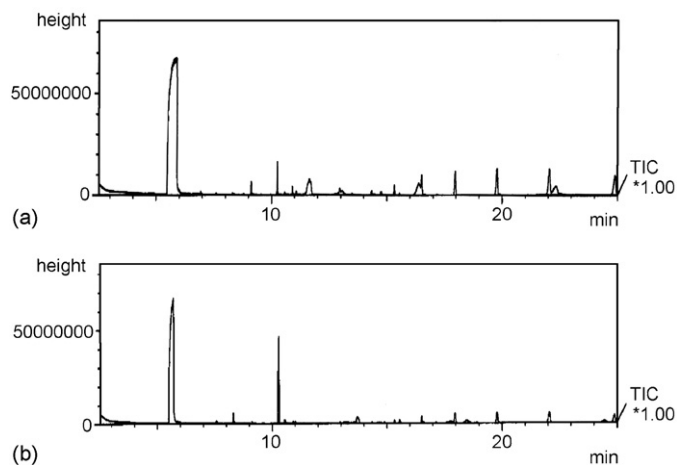
Fig. 2. (a) GC/MS spectra of an irradiated mixture of 4-bromoaniline (1) in aqueous suspension of titanium dioxide. (b) GC/MS spectra of an irradiated mixture of 4-bromoaniline (1) in aqueous suspension of titanium dioxide.

and mass fragmentation pattern (indicated below) with those reported in the GC–MS library.

- Compound 7: m/z, 173 (M^+), 156, 143, 117, 106, 92, 74, 65, 46 and 40.
- Compound 11: m/z, 202 (M^+), 185, 171, 155, 143, 129, 117, 105, 92, 75, 63 and 50.
- Compound 13: m/z, 340 (M^+), 236, 183, 155, 152, 129, 102, 90, 76, 63, 50 and 39.

The formation of products 7, 11 and 13 from 1 involving electron transfer reactions, the reaction with hydroxyl radicals and superoxide radical anions formed during the photo-oxidation process, could be understood in terms of the pathways shown in Scheme 1. The model compound 1, on irradiated aqueous TiO_2 may either undergo attack of an $OH^\bullet$ radical on the carbon containing NH_2 group to give radical species 6 or may lose an electron from the nitrogen of NH_2 group to give a radical cation species 8. The intermediate species 6 may give rise to the observed product 7 on loss of a molecule of NH_3. The radical cation species 8 may lose a H^+ to give a radical species 9 which may either undergo dimerization followed by oxidation to give the observed product 13, or may undergo attack of an $OH^\bullet$ radical ultimately leading to product 11.

3.2. Photocatalysis of TiO_2 suspension containing 3-nitroaniline (2)

The irradiation of 3-nitroaniline (2, 1 mM) in water for 2 h in the presence of TiO_2 (Degussa P25, 1 g L^{-1}) and work up of the reaction mixture under analogous conditions followed by GC–MS analysis of the residue (as illustrated in Fig. 3) showed the formation of 2-amino-4-nitrophenol (15) appearing at retention time (t_R) 10.5 min. The product was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, indicated as follows: compound 15: m/z, 154 (M^+), 138, 124, 108, 96, 80, 63 and 57.
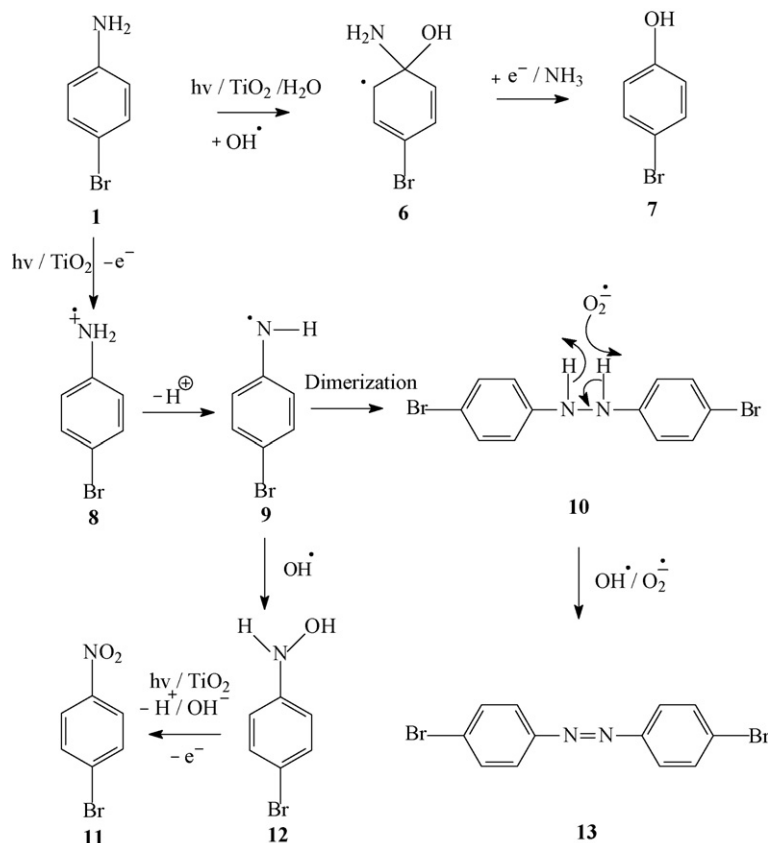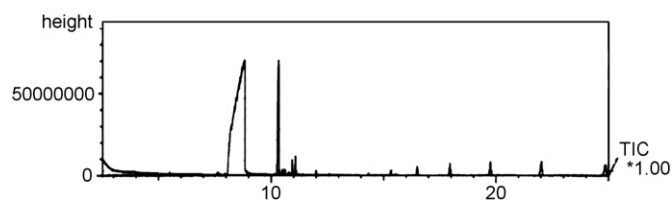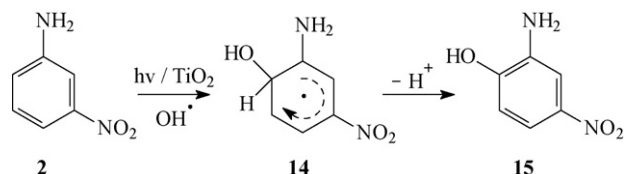

Scheme 1.

Fig. 3. GC/MS spectra of an irradiated mixture of 3-nitroaniline (**2**) in aqueous suspension of titanium dioxide.
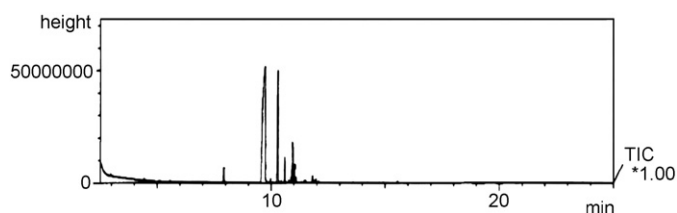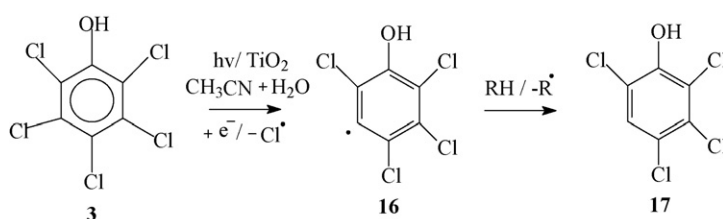

Scheme 2.

Fig. 4. GC/MS spectra of an irradiated mixture of pentachlorophenol (**3**) in aqueous suspension of titanium dioxide.
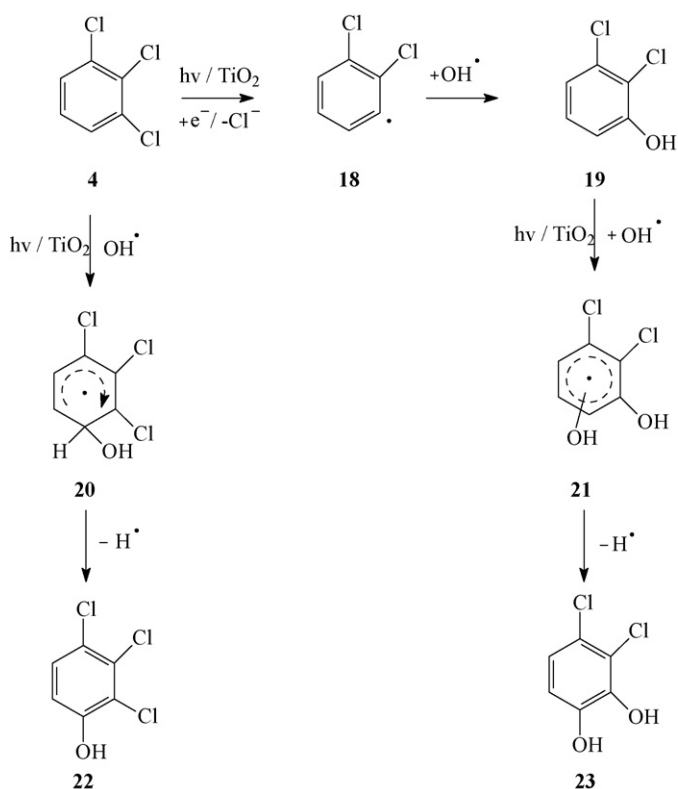

Scheme 4.

The formation of product **15** from **2** involving attack of hydroxyl radicals formed in the photocatalytic system could be understood in terms of pathways shown in Scheme 2. The model compound **2**, on irradiated aqueous TiO$_2$ may undergo attack of an OH$^\bullet$ radical to give a radical species **14** which on subsequent removal of a proton gives the observed product **15**.

3.3. Photocatalysis of TiO$_2$ suspensions containing pentachlorophenol (**3**)

A solution of pentachlorophenol (**3**, 2 mM) in 1:1 acetonitrile/water mixture was irradiated for 12 h in the presence of TiO$_2$ (Degussa P25, 1 g L^{-1}) and worked up under analogous conditions. The GC–MS analysis of the irradiated mixture showed the formation of several products (Fig. 4), of which one of the photoproducts was identified as 2,3,4,6-tetrachlorophenol (**17**) appearing at (t_R) 7.9 min along with some unchanged starting material **3** appearing at (t_R) 9.7 min. The product was identified on the basis of molecular ion and mass fragmentation pattern with those reported in the GC–MS library, indicated as follows:

compound **17**: *m/z*, 232 (*M*$^+$), 194, 166, 143, 131, 116, 96, 65 and 47.

The formation of photoproduct **17** from **3** could be arising through the transfer of an electron followed by loss of chloride ion with subsequent abstraction of a hydrogen atom as shown in Scheme 3.

3.4. Photocatalysis of TiO$_2$ suspensions containing 1,2,3-trichlorobenzene (**4**)

The irradiation of 1,2,3-trichlorobenzene (**4**, 2 mM) in 1:3 acetonitrile/water mixture for 5 h in the presence of TiO$_2$ (Degussa P25, 1 g L^{-1}) and work up of the reaction mixture under analogous conditions followed by GC–MS analysis of the irradiated mixture showed the formation of several products. Two products such as 2,3,4-trichlorophenol (**22**) and 3,4-dichlorobenzene-1,2-diol (**23**) appearing at (t_R) 6.3 and 6.1 min have been identified by comparing the molecular ion and mass fragmentation pattern (mentioned below) with those reported in the GC–MS library.

Scheme 3.

- Compound **22**: *m/z*, 198 (*M*⁺), 160, 132, 99, 73, 62, 48 and 37.
- Compound **23**: *m/z*, 178 (*M*⁺), 142, 132, 114, 99, 86, 79, 62 and 50.

Probable mechanisms for the formation of photoproducts **22** and **23** from **4** involving electron transfer reactions and reaction with hydroxyl radicals is shown in Scheme 4.

3.5. Photocatalysis of TiO₂ suspensions containing diphenylamine (5)

A solution of diphenylamine (**5**, 0.2 mM) in 1:3.5 acetonitrile/water mixture was irradiated for 1 h in the presence of TiO₂ (Degussa P25, 1 g L⁻¹) and worked up under analogous conditions. The GC–MS analysis of the irradiated mixture showed the formation of several products, as shown in Fig. 5, of which three products such as 4-(phenylamino) phenol (**27**), carbazole (**28**) and aniline (**31**) appearing at (*t*ᵣ) 10.3, 9.7 and 12.9 min, respectively, were identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC–MS library, as indicated below:
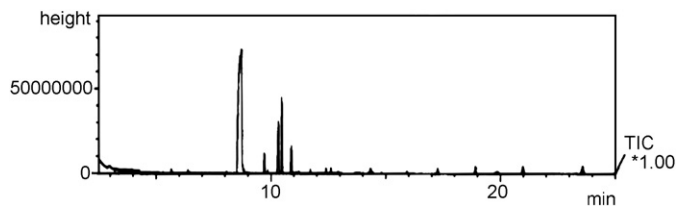

Fig. 5. GC/MS spectra of an irradiated mixture of diphenylamine (**5**) in aqueous suspension of titanium dioxide.

- Compound **27**: *m/z*, 185 (*M*⁺), 168, 156, 129, 115, 108, 91, 77, 65, 51 and 39.
- Compound **28**: *m/z*, 167 (*M*⁺), 139, 113, 98, 86, 83, 69, 50 and 39.
- Compound **31**: *m/z*, 93 (*M*⁺), 78, 66, 52 and 39.

A probable mechanism for the formation of products **27**, **28** and **31** from **5** involving electron transfer reactions, reaction with hydroxyl radical and superoxide radical anion formed during the photo-oxidation process, could be understood in terms of the pathways shown in Scheme 5(a) and (b), respectively. The formation of carbazole derivative, **28** could be arising through
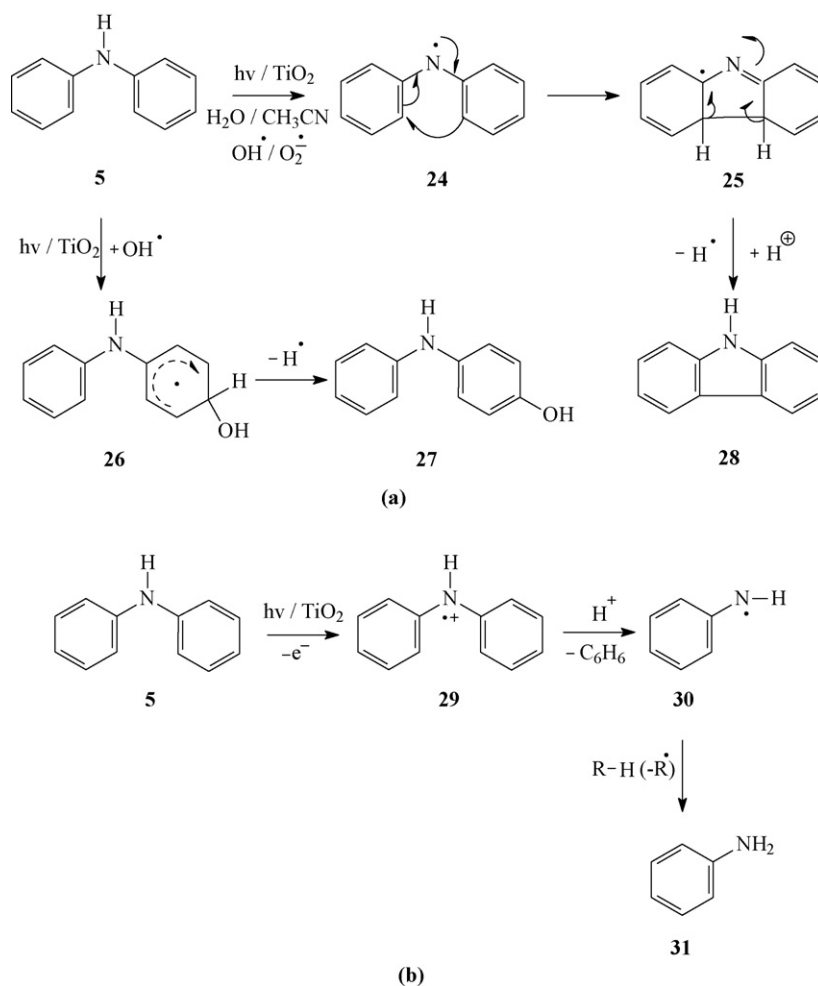
Scheme 5.

the abstraction of hydrogen atom either by $OH^{\bullet}$ or $O_2^{\bullet-}$ to give a radical species, **24**, which may undergo cyclization followed by aromatization. The hydroxylated product, **27** and cleavage product, **31** take a common reaction pathway under the reaction conditions.

4. Conclusion

The present article deals with more experimental evidence based on GC/MS analyses, in support of earlier discussed possibility of direct hole-oxidation of the model compounds and the $OH^{\bullet}$ mediated degradation route by detecting different photo-oxidation products. The identification and characterization of the different intermediate products formed during the photo-oxidation process is a useful source of information for various organic syntheses and also from a mechanistic point of view.

Acknowledgment

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