

# Photoinduced electron transfer reaction of few selected organic systems in presence of titanium dioxide

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## Abstract

In an attempt to improve our understanding of the basic mechanisms of the degradation of aromatic pollutants, the photocatalysed reactions of five selected organic systems, namely 2-naphthoic acid (**1**), 2,6-dichloro-4-nitro aniline (**2**, dichloran), 4-nitro phenyl acetate (**3**), 1,3-diallyl-2-thio-urea (**4**), and 7-hydroxy-4-methyl coumarin (**5**) has been investigated in water or acetonitrile/water mixture in the presence of titanium dioxide and oxygen. An attempt has been made to identify the products formed during the photooxidation process through GC/MS analysis technique. The photolysis of 2-naphthoic acid (**1**) showed the formation of 2-formylcinnamaldehyde (**11**) and 1,2-benzenedicarboxaldehyde (**13**) whereas 2,6-dichloro-4-nitro aniline (**2**) gave rise to 2,6-dichloro-4-nitro phenol (**14**). However, the photolysis of 4-nitro phenyl acetate (**3**) yielded 4-nitrophenol (**15**). The illumination of 1,3-diallyl-2-thio-urea (**4**), on the other hand, led to the formation of 1,3-diallyl urea (**19**). Product 2,4-dihydroxy acetophenone (**25**) was identified in case of 7-hydroxy-4-methyl coumarin (**5**). The products have been identified by comparing the molecular ion and mass fragmentation peaks of the products with those reported in the GC–MS library. 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<sub>2</sub> has become a subject of serious study as it shows promise in becoming a viable commercial technology for the wastewater treatment [1–5]. 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<sub>2</sub> [6].

Generally, semiconductor-mediated photocatalysis involves photoexcitation 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• radical mediated reactions, the current prevailing view favors the latter [7]. 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 [8–10].

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It may be used as an alternative method for selective organic synthesis under environmentally benign conditions and aid the pollution reduction by eliminating potential wastes at their source. Such heterogeneous photocatalysis has been carried out both in organic solvents (usually acetonitrile) [11–18] and in aqueous suspensions [19–26] and also in acetonitrile/water mixture [27].

We, therefore, chose to study the photocatalysed reaction of 2-naphthoic acid (**1**), 2,6-dichloro-4-nitro aniline (**2**, dichloran), 4-nitro phenyl acetate (**3**), 1,3-diallyl-2-thio-urea (**4**) and 7-hydroxy-4-methyl coumarin (**5**) with an aim to identify the intermediate products formed during the photooxidation process.

## 2. Experimental section

### 2.1. Reagents

2-Naphthoic acid and dichloran were obtained from Fluka, 4-nitro phenol and 1,3-diallyl-2-thio-urea were obtained from BDH, England, whereas, 7-hydroxy-4-methyl coumarin was synthesized. Reagent grade acetonitrile and double distilled water were employed 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  $50 \text{ m}^2 \text{ g}^{-1}$  and a primary particle size of 20 nm [28,29].

### 2.2. Procedure

The desired concentration of the compound was dissolved in appropriate acetonitrile/water mixture or water and taken in an immersion well photochemical reactor made of Pyrex glass (250 mL capacity). The required amount of photocatalyst was added and irradiated using 125 W medium-pressure mercury lamp with continuous stirring and purging with molecular oxygen. 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 analysed by GC/MS. For GC/MS analysis a Shimadzu gas chromatograph and mass spectrometer (GCMS-QP 5000) equipped with a 25 m CP SIL 19 CB ( $d = 0.25 \text{ mm}$ ) capillary column, operating temperature programmed (injection temperature, column temperature,  $260^\circ\text{C}$  for 53 min at the rate of  $10^\circ\text{C min}^{-1}$ ) in split mode, injection volume ( $1.0 \mu\text{L}$ ) with helium as a carrier gas was used.

## 3. Results and discussion

### 3.1. Photolysis of $\text{TiO}_2$ suspensions containing 2-naphthoic acid (**1**)

A solution of 2-naphthoic acid (**1**, 1 mM) in acetonitrile/water mixture (1:1) was irradiated with a 125 W

medium-pressure mercury lamp in presence of Degussa P25 ( $1 \text{ g L}^{-1}$ ) for 3 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, showed the formation 2-formylcinnamaldehyde (**11**) and 1,2-benzenedicarboxaldehyde (**13**) appearing at retention times ( $t_R$ ) 7.335 and 7.707 min respectively. The products were identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, which are indicated below:

- Compound **11**:  $m/z$ , 160 ( $M^+$ ), 149, 132, 121, 105, 84, 77, 65, 51 and 40.
- Compound **13**:  $m/z$ , 134 ( $M^+$ ), 105, 86, 77, 63, 51 and 40.

The formation of products **11** and **13** from **1** involving electron transfer reactions, reaction with hydroxyl radicals and superoxide radical anions formed during the photooxidation process could be understood in terms of the pathways shown in Scheme 1.

It is pertinent to mention here that the formation of 2-formylcinnamaldehyde (**11**) has been reported earlier from naphthalene (**6**) and similar pathway was proposed [30,31].

### 3.2. Photolysis of $\text{TiO}_2$ suspensions containing dichloran (**2**)

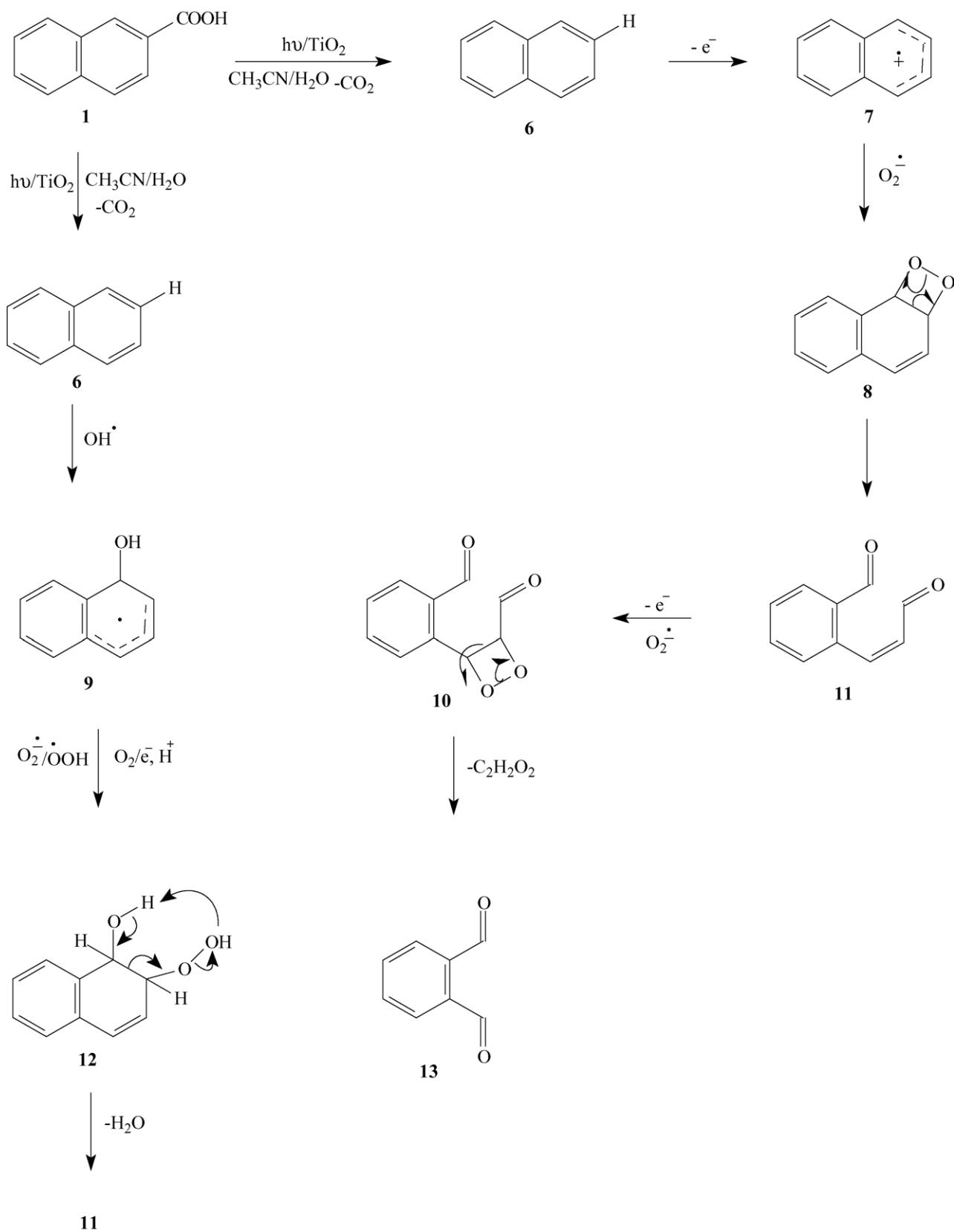
The irradiation of 2,6-dichloro-4-nitro aniline (**2**, 0.5 mM) in 3:2 acetonitrile/water mixture for 6 h in presence of Degussa P25 ( $1 \text{ g L}^{-1}$ ) and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the irradiated mixture showed the formation of 2,6-dichloro-4-nitro phenol appearing at retention time ( $t_R$ ) 10.237 min. The product was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

- Compound **14**:  $m/z$ , 211 ( $M^+$ ), 177, 161, 141, 133, 125, 99, 97, 73, 62 and 53.

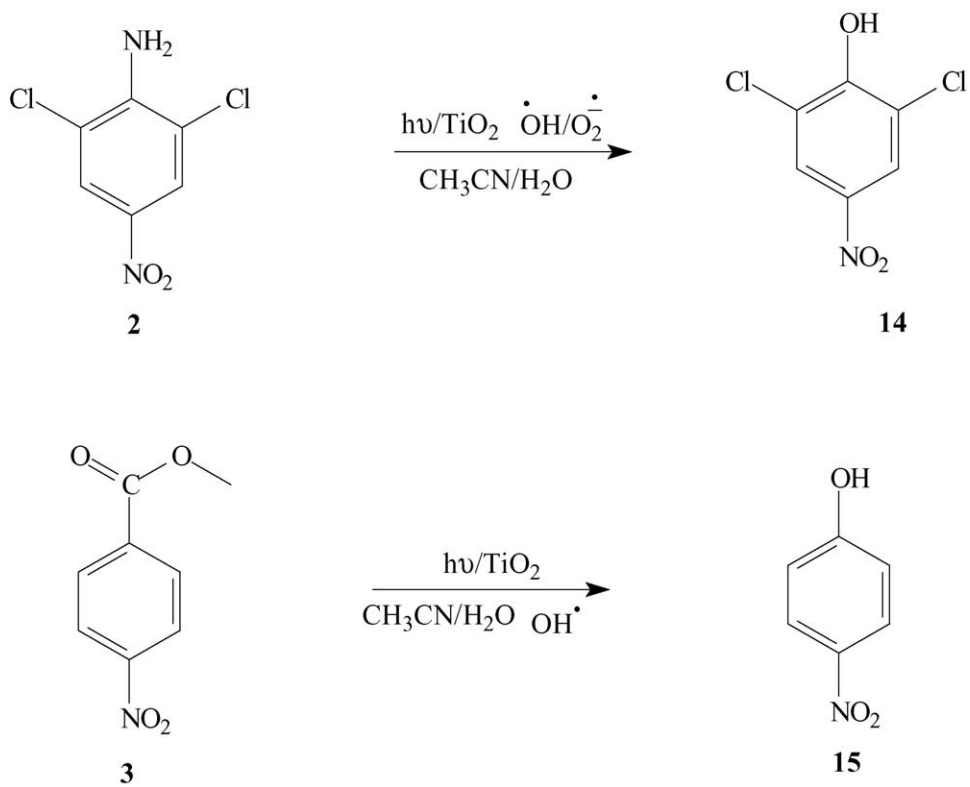
### 3.3. Photolysis of $\text{TiO}_2$ suspensions containing 4-nitro phenyl acetate (**3**)

The irradiation of 4-nitro phenyl acetate (**3**, 0.5 mM) in 1:1 acetonitrile/water mixture for 2 h in presence of Degussa P25 ( $1 \text{ g L}^{-1}$ ) and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the irradiated mixture showed the formation of 4-nitro phenol appearing at retention time ( $t_R$ ) 7.705 min. The product was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

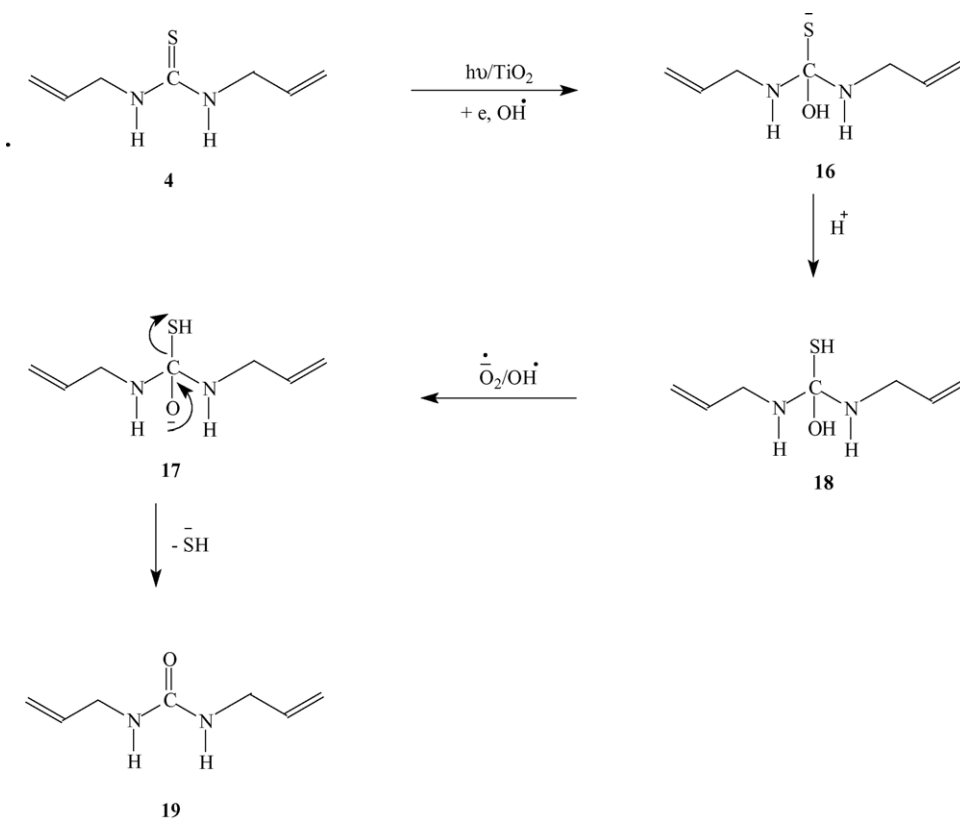
- Compound **15**:  $m/z$ , 140 ( $M^+$ ), 139, 123, 109, 93, 81, 65, 53 and 39.



Scheme 1.



Scheme 2.

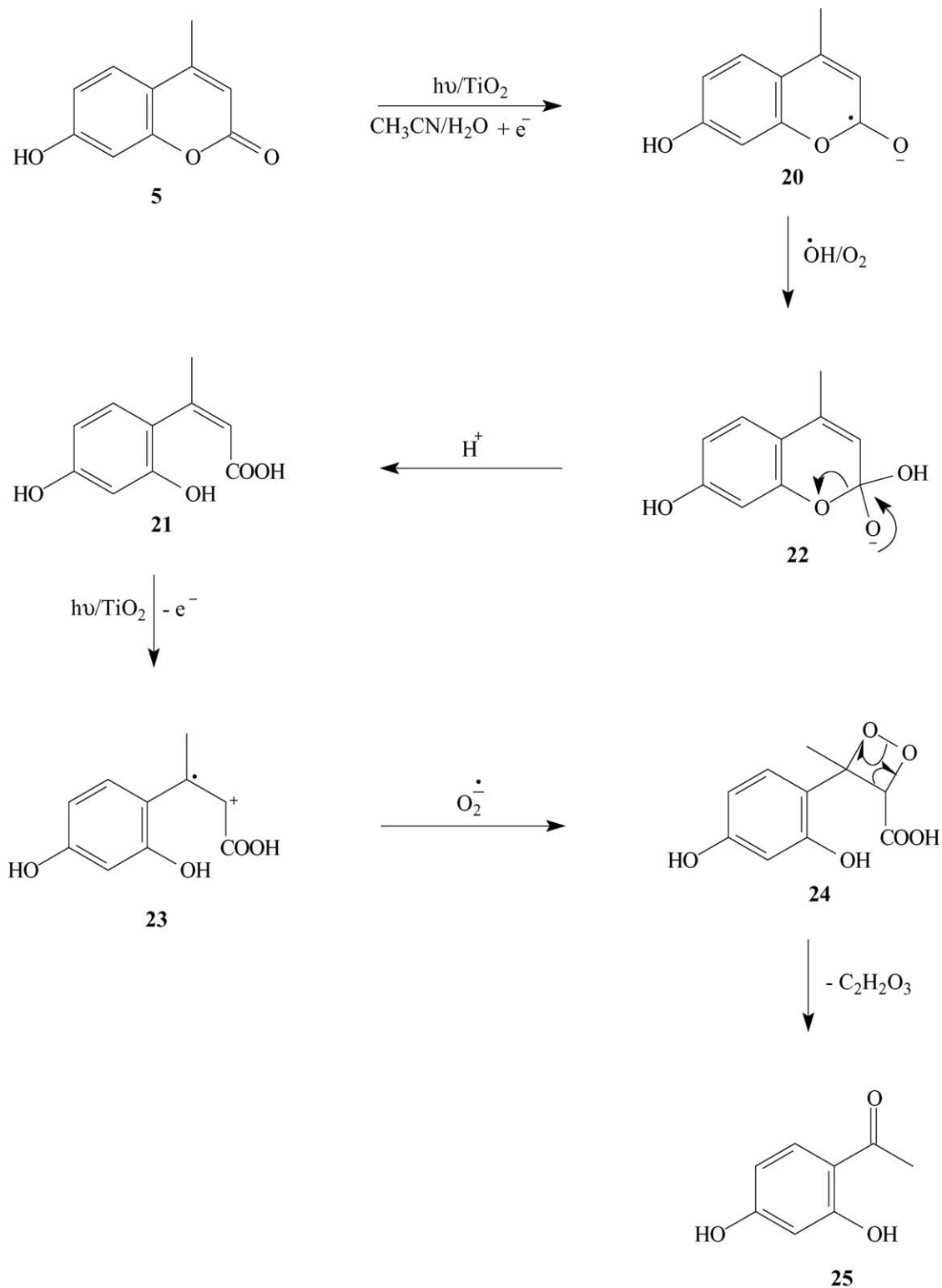


Scheme 3.

The compounds, dichloran (**2**) as well as 4-nitro phenyl acetate (**3**), undergo substitution reaction. In case of **2**, amino group is replaced by hydroxy group whereas in case of **3**, acetate group is preferred to be replaced by hydroxy group as illustrated in Scheme 2.

### 3.4. Photolysis of $\text{TiO}_2$ suspensions containing 1,3-diallyl-2-thio-urea (**4**)

The irradiation of 1,3-diallyl-2-thio-urea (**3**, 1 mM) in aqueous suspension of  $\text{TiO}_2$  ( $1 \text{ g L}^{-1}$ ) and work up of the



Scheme 4.

reaction mixture under analogous conditions followed by GC/MS analysis of the irradiated mixture showed the formation of 1,3-diallyl urea appearing at retention time ( $t_R$ ) 5.807 min. The product was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

- Compound **19**:  $m/z$ , 139 ( $M^+$ ), 125, 98, 83, 56, 54 and 41.

A wide variety of compounds have been found to oxidize on illuminated semiconductor particles [32]. Only a few of them, however, can be stopped at the stage when the desired product is formed without incurring further reactions. In particular, the photoinduced oxidation of aryl systems has been studied [14]. The  $TiO_2$  photocatalysed oxidative cleavage of aryl olefins gives rise, in excellent chemical yields, to carbonyl compounds by initial oxygenation of double bond. In such an oxidation, oxygen is always used as electron acceptor to scavenge the conduction band electron. The radical species such as superoxide radical anion may also act as oxidant.

Here, we report our investigation of the photocatalysed oxygenation of 1,3-diallyl-2-thio urea in which initial oxygenation of  $>c=s$  to  $>c=o$  is observed. A possible formation of the product has been outlined in Scheme 3.

### 3.5. Photolysis of $TiO_2$ suspensions containing 7-hydroxy-4-methyl coumarin (**5**)

The photolysis of 7-hydroxy-4-methyl coumarin (**5**) in 1:1 acetonitrile/water mixture was carried out for 2.5 h and work up of the reaction mixture under analogous conditions followed by GC/MS analysis of the extract of the solution showed the formation of several intermediate products of which 2,4-dihydroxy acetophenone (**25**) appearing at retention time ( $t_R$ ) 7.800 min was identified by comparing the molecular ion and mass fragmentation pattern with those reported in the GC/MS library, as indicated below:

- Compound **25**:  $m/z$ , 152, 137, 123, 109, 95, 81, 69 and 43.

The formation of product **25** from **5** involving electron transfer reactions, reaction with hydroxyl radicals and superoxide radical anions formed during the photooxidation process could similarly be understood in terms of the pathways shown in Scheme 4.

The parent compound **5** may accept an electron to give radical anion **20** which can lead to the formation of ring cleaved product **21** either by the reaction of hydroxyl radical or  $O_2$  followed by protonation. This species may further lose an electron to give rise radical cation **23**, which may finally produce the observed product **25** by the coupling with superoxide radical anion followed by rearrangement.

## 4. Conclusion

Heterogeneous photocatalysis involves electron hole-pair formation initiated by band gap excitation of a semiconductor

particle. Photocatalysis, a widely applicable method for activating adsorbed organic molecules, is promising as a route to various synthetic transformations or as an advanced oxidation process for environmental cleanup. The present paper 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 photooxidation products. The identification and characterization of the different intermediate products formed during the photooxidation process is a useful source of information for various organic syntheses and also from mechanistic point of view.

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