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Photocatalyzed reaction of indole in an aqueous suspension of titanium dioxide

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Abstract The photocatalyzed oxidation of indole (**1**) in an aqueous suspension of titanium dioxide has been investigated and an attempt has been made to identify the products formed during the photooxidation process by gas chromatographic–mass spectrometric (GC–MS) analysis. Photolysis of an aqueous solution of indole (**1**) in the presence of titanium dioxide and oxygen led to the formation of 2,3-dihydro-indole-2-one (**6**) and 1*H*-indole-2,3-dione (**7**). A probable pathway for the formation of these products has been proposed.

Keywords Photocatalytic oxidation · Photocatalysis · Indole · Titanium dioxide · Semiconductor

Introduction

The photocatalyzed reaction of organic molecules in the presence of semiconductors such as TiO_2 has become a subject of serious study as it shows promise in becoming a viable commercial technology for wastewater treatment [1–5]. This process bears a close similarity to the charge separation developed in a photochemical cell, containing semiconductor electrodes and the principles governing photoelectrochemistry apply equally well to reactions occurring on the surface of irradiated

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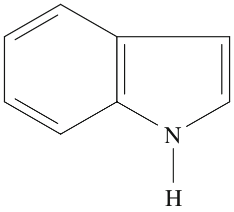
particles [6]. On irradiation of the semiconductor at appropriate wavelengths an electron is excited from the valence band to the conduction band, yielding an electron/hole pair. The reaction of this electron–hole pair with a variety of electron acceptors and donors, and the electron–hole recombination processes, have been well studied [7, 8]. The formation of cation radicals of organic substrates, following electron transfer to the excited semiconductor has been unambiguously characterized both from product analysis [9] and by spectroscopic studies [10]. The trapped hole in TiO_2 can lead to the formation of hydroxyl radicals, which can abstract a hydrogen atom from weak C–H bonds and reacts with multiple bonds, including reactions with aromatic systems, leading to the formation of free radicals. In the presence of oxygen, these free radicals can be rapidly converted into unstable peroxy radicals. Subsequent reactions of the peroxy radicals and other intermediates formed can lead to the oxidation of organic materials dissolved in water. Of the two possible pathways for the initial oxidation reactions namely, that involving direct oxidation of organic substrate and the other proceeding through $OH^{\bullet}$ radical-mediated reactions, the current prevailing view favors the latter [11]. 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. Recent pulse radiolysis studies seem to suggest that the surface-trapped hole and surface bound $OH^{\bullet}$ radicals may be indistinguishable [12].

The redox reactions of variety of organic molecules in acetonitrile have been reported earlier [13–17] but very few reactions in aqueous systems have been reported. For example, an aqueous suspension of 1,4-dihydrofuran in the presence of zinc sulfide undergoes oxidation to give the coupling product [18–21].

An earlier study [22] has shown that the reaction of indole in the presence of cadmium sulfide gives interesting products. In order to look into the nature of products formed in the presence of titanium dioxide, we have studied the photocatalyzed reaction of indole in an aqueous suspension of TiO_2.



(1)

Experimental

Reagents

Reagent-grade indole was obtained from Merck and used as received without further purification. Double-distilled water was employed for irradiation experiments. P25 from Degussa was used as photocatalyst in this study. 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 [23, 24].

Procedure

The model compound was dissolved in water and placed in an immersion well photochemical reactor made of Pyrex glass (250 ml capacity). The required amount of photocatalyst (Degussa P25, 1 g L^{-1}) was added and irradiated using a 125-W medium-pressure mercury lamp, with continuous stirring and purging with molecular oxygen. The irradiated mixture was centrifuged and extracted with chloroform, and the extract was subsequently dried over anhydrous sodium sulfate. Removal of the solvent under reduces pressure gave a residual mass 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. The column oven temperature was programmed from 53 to 260 °C at 10° min^{-1}). Injection was in split mode (injection volume 1.0 μL), and helium was used as carrier gas.

Results and discussion

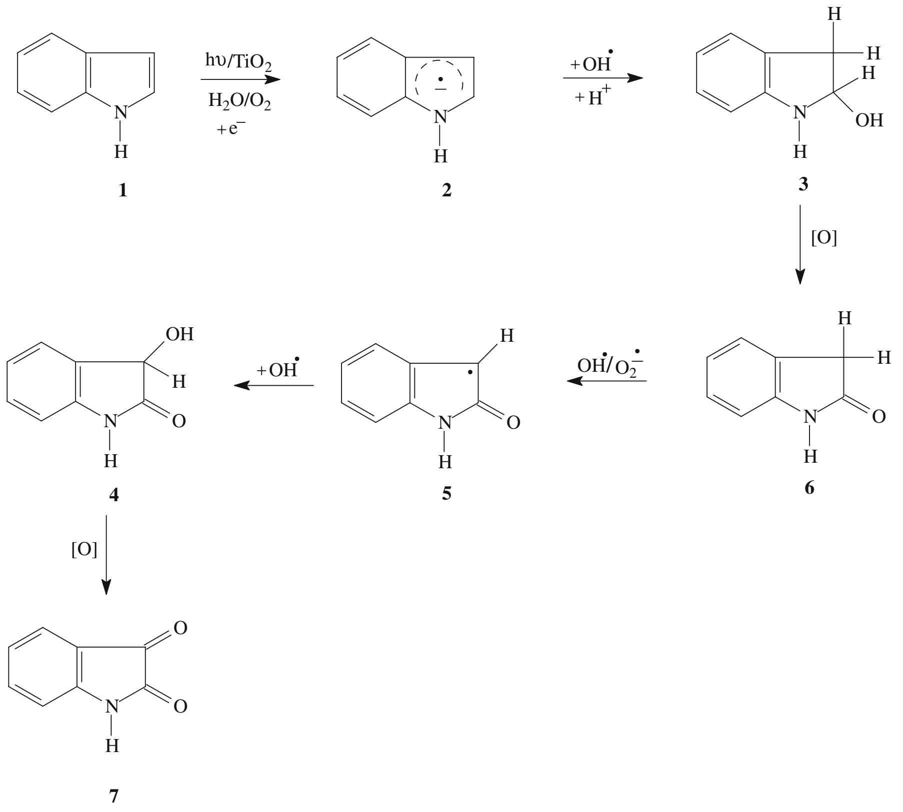
An aqueous solution of indole (**1**, 2 mM) was irradiated with a 125-W medium-pressure mercury lamp in the presence of Degussa P25 (1 g L^{-1}) and oxygen for 2 h. The catalyst was removed, the aqueous solution was extracted with chloroform, the extract was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure to give a residual mass. GC–MS analysis of the residue revealed the formation of 2,3-dihydroindole-2-one (**6**) appearing at retention time (t_R) 8.02 min. Prolonged irradiation of the model compound for 4 h (with work up of the reaction mixture under analogous conditions) resulted in the formation of an addition product appearing at retention time (t_R) 10.55 min; this was identified as 1*H*-indole-2,3-dione (**7**). The products were identified by comparing their molecular ions and mass fragmentation patterns (indicated below) with those reported in the GC–MS library.

Compound **6**: *m*/*z*, 133 (M^+), 104, 89, 78, 63, 51, and 41

Compound **7**: *m*/*z*, 147 (M^+), 119, 104, 92, 76, 64, 50, 45, 41, and 38

Highly regioselective oxidation of the carbon near a heteroatom, for example oxygen and nitrogen, has been accomplished on illuminated semiconductor particles. For example, formation of benzoate esters by photooxidation of benzyl ethers [17] and imides from lactams and *N*-acylamines in the presence of TiO_2 [25].

The formation of products **6** and **7** from **1** involving electron-transfer reactions, reaction with hydroxyl radicals and superoxide radical anion, formed in the photocatalytic system, could be understood in terms of the pathways shown in Scheme 1. The model compound **1** upon transfer of an electron can form the radical anion **2**, which may undergo addition of a hydroxyl radical followed by abstraction of a proton to give **3**. This compound, on oxidation under these reaction conditions, can lead to the formation of the observed product **6**. The abstraction of a hydrogen



Scheme 1

atom from **6**, either by a hydroxyl radical or by a superoxide radical anion, can form the radical species **5**, which on subsequent addition of a hydroxyl radical followed by oxidation can lead to the formation of the observed product **7**.

Conclusion

Photocatalysis of indole in an aqueous suspension of titanium dioxide has been found to result in oxidation at the 2 and 3 positions to yield two oxidized products. Identification and characterization of the products formed during the photooxidation process was a useful source of mechanistic information.

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