



Substituent effect in photocatalytic oxidation of 2-oxo-1,2,3,4-tetrahydropyrimidines using TiO₂ nanoparticles

Hamid R. Memarain*, Mahnaz Ranjbar

Catalysis Division, Department of Chemistry, University of Isfahan, 81746-73441 Isfahan, Islamic Republic of Iran

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Dedicated to Prof. Dietrich Döpp on occasion of his 75th birthday.

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ABSTRACT

The semiconductor-sensitized oxidation of various 1-, 4- and 5-substituted 2-oxo-1,2,3,4-tetrahydropyrimidines was carried out in acetonitrile using TiO₂ anatase nanoparticles. The aims of this study were to elucidate the effects of the nature of the substituents on the 1-, 4- and 5-positions of the heterocyclic ring, the type of the photocatalyst and the nature of solvent on the rate of reaction. The proposed electron-transfer mechanism is supported by the experimental results and also by the computational studies.

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1. Introduction

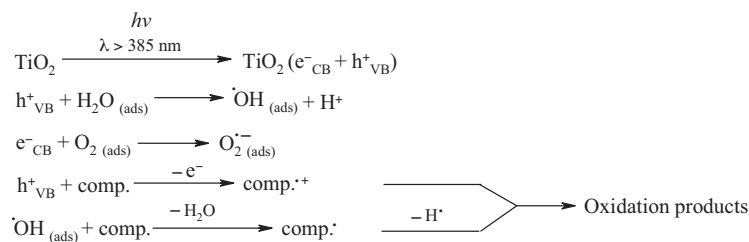
Photochemical oxidation (PCO) is a promising technology which utilizes semiconductor powders; mainly metal oxides such as TiO₂, ZnO, WO₃ suspended in solution or as supported thin film to carry out a light-induced redox process for oxidation of various chemicals [1,2]. TiO₂ is the most extensively used semiconductor photocatalyst because of its photocatalytic activity, chemical stability, non-toxicity and low cost. TiO₂ has been widely used for degradation of various contaminants such as azo dyes [3–5], ammonia [6], cyanide [7], benzonat as a herbicide [8] or by photo-oxidation of aryl alcohols [9], α,β -dihydroxybenzyl derivatives [10–12] or organic sulfides [13]. When TiO₂ is subjected to UV light ($\lambda \geq 385$ nm), the primary step following the light absorption is the excitation of an electron from the TiO₂ valence band to the conduction band producing an electron/hole pair (e_{CB}^-/h_{VB}^+), which must be trapped somehow in order to avoid recombination (Scheme 1).

The redox process takes place primarily on the surface of TiO₂, where the photogenerated electrons and holes may interact with

electron-acceptor or electron-donor species present in the medium [14]. The photogenerated holes are also able to accept an electron from adsorbed water producing hydroxyl radical (when the experiment is being carried out in aqueous media), or from the compound to be oxidized which is present in the solution. Meanwhile, oxygen dissolved in solution can scavenge the excited electrons, limiting the electron-hole recombination by formation of superoxide radical ($O_2^{\bullet-}$), which acts as an active oxidant or reductant [15].

2-Oxo-1,2,3,4-tetrahydropyrimidines (THPMs) are important compounds due to their biological activities such as antitubercular [16], antihypertensive [17], antibacterial [18], anticancer agents [19], as calcium channel blockers [20] and inhibitors of the HIV virus [21]. Different activities of these compounds are related to the nature of the substituents located on the 4- and 5-positions of the heterocyclic ring. Recently, we studied the efficient oxidation of THPMs containing acetyl or carboethoxy groups on the 5-position of the heterocyclic ring by potassium peroxydisulfate (K₂S₂O₈) in aqueous acetonitrile under thermal [22], sono-thermal [23,24] and microwave [25] activations. According to the proposed mechanism and considering the results obtained in these studies, we found out that the removal of 4-hydrogen in the rate determining step occurs by *in situ* hydroxyl radical, an active hydrogen-abstracting species, formed in the reaction of potassium sulfate radical and water. This

* Corresponding author. Tel.: +98 311 793 2707; fax: +98 311 668 9732.
E-mail address: memarian@sci.ui.ac.ir (H.R. Memarain).



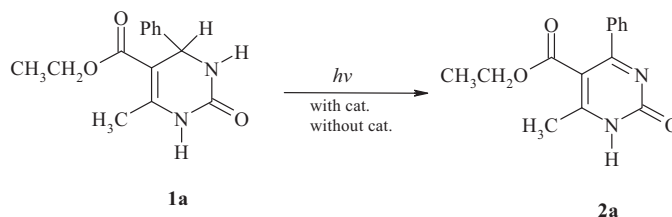
Scheme 1.

argument is supported by the influence of the steric and electronic effects of the substituents attached to C4- and C5-atoms of the heterocyclic ring on the rate of this step. In continuation, we have studied the light sensitivity of 5-carboethoxy- [26] and 5-acetyl-THPMs [27] in the electron-transfer induced photo-oxidation in chloroform. These results explain an electron-transfer process from excited THPMs to CHCl_3 and reconfirming the effect of the nature of these substituents on the rate of oxidation. The results of photochemical studies lead us to extend our investigations concerning the interaction of THPMs containing various substituents at 1-, 4- and 5-positions of the heterocyclic ring toward photo-excited TiO_2 anatase nanoparticles. The results should elucidate the effects of the nature and steric hindrance of the substituent on the rate of reaction.

2. Experimental

The THPMs were prepared according to the known procedure [28]. Titanium(IV) dioxide, anatase nanopowder (99.7%), anatase powder (99.9+%) and rutile powder (99.9+%) were purchased from Aldrich, and Degussa P-25 was purchased from Degussa, Germany. Melting points were determined on a Stuart Scientific SMP2 apparatus and are not corrected. IR spectra were recorded using KBr pellets on a Jasco FT/IR-6300 spectrometer. The ^1H and ^{13}C NMR spectra (DMSO- d_6) were recorded on a Bruker DRX-300 Avance and Bruker Avance III 400 spectrometers at 300, 400, 75.47, and 100.62 MHz. The ^1H NMR spectra are reported as follows: chemical shifts [multiplicity, number of protons, coupling constants J (Hz), and assignment]. Mass spectra were obtained on Platform II Mass Spectrometer from Micromass; EI mode at 70 eV. UV spectra were taken (in CH_3CN) with Shimadzu UV-160 spectrometer. All irradiations were carried out using a 400 W high-pressure Hg lamp from NARVA in Duran glass equipment, which was placed in a distance of 20 cm from light source.

The TiO_2 suspension (0.3 g TiO_2 anatase nanoparticles in 10 mL dry acetonitrile) was sonicated for 15 min to disperse TiO_2 uniformly in the solution. 100 μL of this suspension was added to solution of 0.01 mmol of THPM in 10 mL dry solvent, then the solution was magnetically stirred in the dark until a homogenous suspension was obtained. After that, the solution was irradiated with stirring until total disappearance of THPM. It should be noted that for the preparative scale, a solution of 0.1 mmol of THPMs and 12.5×10^{-2} mmol of TiO_2 anatase nanoparticles in 100 mL acetonitrile was irradiated until total disappearance of THPM. The mixture was centrifuged to remove TiO_2 effectively. The solution was separated by careful filtration; the solid material was washed with acetonitrile. Solvent was evaporated and the residue was recrystallized from *n*-hexane/ethyl acetate (otherwise is mentioned) to afford pure product. The known products were identified by comparison of their melting points and spectral data with those of the authentic samples. The physical and the spectral data of the new THPMs and the corresponding DHPMs are given as [supplementary material](#).



Scheme 2.

3. Results and discussion

3.1. Photocatalyst activity and optimization of the reaction condition

In order to find a suitable form of TiO_2 for the electron-transfer induced oxidation of various THPMs, the solutions containing 0.01 mmol of ethyl 2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidin-5-carboxylate (**1a**) as a test substrate in dry acetonitrile in the absence of the photocatalyst or in the presence of 3.75×10^{-3} mmol of each of the photocatalysts anatase, rutile, Degussa P-25 (a mixture of 70% anatase and 30% rutile phases) and anatase nanoparticles were irradiated until maximum conversion of **1a** to **2a** (Scheme 2). The results shown in Fig. 1 indicated that the complete conversion of **1a** in shorter reaction time is observed using TiO_2 anatase nanoparticles, while irradiation in the presence of TiO_2 (anatase) and TiO_2 (rutile) resulted in 50% and 15% conversion of **1a**, respectively, and Degussa P-25 causes 90% conversion after the same irradiation time (3.75 h). Even though anatase should be the most active form of TiO_2 , but some reports suggest that the presence of rutile phase with anatase introduces wider pore size distribution [29], this may be the cause of higher conversion observed using Degussa P-25. The effect of the particle size on the photocatalytic activity can be interpreted in terms of surface area. Generally, the smaller the particle size, the larger the surface area

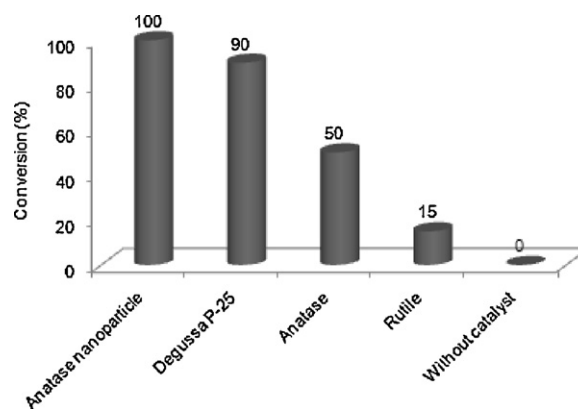


Fig. 1. The effect of TiO_2 -type on the rate of photo-oxidation of **1a** after 3.75 h photolysis.

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