

An investigation of the effects of Cu^{2+} and heat treatment on TiO_2 photooxidation of certain pyrimidines

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Received 7 July 1999; received in revised form 13 October 1999; accepted 20 January 2000

Abstract

An unusual observation of rate retarding influence of Cu^{2+} on the TiO_2 -mediated photooxidation of uracil, thymine and 6-methyluracil has been made. This is explained on the basis of a short-circuiting redox role of Cu^{2+} in the photoprocess. Increase of calcination temperature of the TiO_2 sample resulted in a decrease of its photocatalytic activity and also the extent of its UV absorption. The former effect is attributed to a decreased extent of TiO_2 surface bound peroxy species while the latter is attributed to a decrease in the surface area of TiO_2 . © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heat treatment; Pyrimidines; Photooxidation

1. Introduction

Studies involving semiconductor-mediated photocatalytic reactions of a number of compounds have appeared frequently in Refs. [1–5]. In view of the reported damaging nature of interaction of ultrafine TiO_2 particles on DNA, the present work focuses on the TiO_2 -promoted photoreactions of certain pyrimidines which are the essential constituents in DNA. The free radical ($\cdot\text{OH}$, etc.) activity associated with TiO_2 -assisted photoreactions makes the present work more relevant as a model to probe the TiO_2 particle–DNA interactions also involving free radicals [6,7]. It may be noted that already

we have published some results concerning the TiO_2 -promoted photooxidation of certain pyrimidine bases which are the constituents of DNA [8]. The influences of Cu^{2+} as a trap for e_{cb}^- (cb = conduction band) [9] formed in the primary step of TiO_2 photocatalysis and heat treatment of TiO_2 on the rate of the reaction have been investigated in this work. The significant role of surface-bound peroxy groups in TiO_2 -assisted photoprocesses is well-established [10]. Heat treatment of the semiconductor samples prior to irradiation is known to largely affect the extent of surface associated peroxy groups, thus leading to a consequent alteration in the rate of overall photoprocess [10]. Hence, in order to gain an insight into the role of this factor, experiments utilizing TiO_2 samples calcined at different temperatures have been carried out in this study.

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2. Experimental section:

The pyrimidines namely uracil, thymine, and 6-methyluracil, NaOH, HClO₄, CuSO₄ and all other chemicals used were of AnalaR (Analytical Reagent) grade. Water, was distilled from a Kilburn still, redistilled over alkaline permanganate in an all-glass vessel and used for solution preparations. The titanium dioxide photocatalyst was Degussa P-25. This material is mainly anatase and has a BET surface area of 50 m² g⁻¹ and a mean particle size of 30 nm.

Irradiations were performed with a medium pressure mercury pencil lamp (Spectronics, USA) emitting nearly 100% at 365 nm. Aqueous suspensions of TiO₂ containing the pyrimidine base in a polymerization tube, with an inlet for O₂ and with constant magnetic stirring, were irradiated for different intervals of time. All the experiments were carried out in the presence of O₂ as a scavenger for e_{cb}⁻ (conduction band electron). The pH of the solutions was measured with a Toshniwal CL 46 pH meter. The progress of the reaction was followed by monitoring the disappearance of the pyrimidine base at 265 nm. The amount of the pyrimidine base decomposed with respect to time was calculated. The rate constants *k* (s⁻¹) were evaluated from plots of log(absorbance) vs. irradiation time (reproducibility of *k* ≈ ±5%), and the initial rates of decomposition of the pyrimidines were calculated by multiplying the rate constants with the appropriate initial pyrimidine concentrations, [pyrimidine]₀. These initial rates were utilized in the calculation of “relative photonic efficiency” (*ζ*), a parameter as suggested by Serpone [11]. The extent of light scattering in a solid/liquid heterogeneous medium is significant. A practical and simple alternative to compare process efficiencies was recently suggested by defining a relative photonic efficiency, (*ζ*). A quantum yield can subsequently be determined from *ζ* since

$$\phi = \zeta \phi_{\text{phenol}}$$

where ϕ_{phenol} is the quantum yield for the photocatalysed oxidative disappearance of phenol

(a standard secondary actinometer) using P-25 TiO₂ as the standard catalyst material [12]. The rationale adopted consists in circumventing the inherent difficulties encountered in the precise evaluation of the number of quanta absorbed by the photocatalyst, difficulties with utilization of different light sources, different reactor geometries and other unspecified factors by referring all the results to an equivalent experiment carried out under identical conditions for a standard process. In defining the term “relative photonic efficiency” (*ζ*), the effects of reactor geometry, light sources and photocatalyst properties are fixed in assessing *ζ* for phenol and for the process of test molecules [13]. It affords comparison of process efficiencies and avoids the confusion with quantum yields in the literature. The relative photonic efficiency was defined as:

$$\zeta = \frac{\text{Initial rate of disappearance of substrate}}{\text{Initial rate of disappearance of phenol}}$$

and these *ζ* can be converted into the photochemically defined quantum yield ϕ once a quantum yield, ϕ_{stand} , for a given photocatalyst and a given substrate has been determined, where

$$\phi = \zeta \phi_{\text{stand}}$$

In this work, the above method has been employed to evaluate ϕ taking the value of ϕ_{stand} for phenol as the standard ($\phi_{\text{stand}} = 0.11$) [11]. The initial photoconversion of phenol was chosen as the standard process and Degussa P-25 titania used in many studies as the photocatalyst [12]. The choice of phenol was due to the fact that the molecular structure of phenol is present in many organic compounds and is degraded essentially by oxidation rather than reduction.

3. Results and discussion

The retarding influence of [Cu²⁺] on the photodegradation rate and the effect of heat treatment (calcination) of the photocatalyst, TiO₂

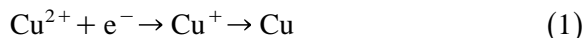
on its reactivity with the above mentioned pyrimidine bases are explained suitably.

4. Effect of $[Cu^{2+}]$

In the present work, a rate retarding role of Cu^{2+} has been noticed. That is, in the range of $[Cu^{2+}]$: 0.25×10^{-5} to 3×10^{-5} mol dm^{-3} , there was a steady decrease in rate (Fig. 1). This is contrary to previous observations. It is well established that the reduction of Cu^{2+} can occur on irradiated TiO_2 surface [14]. In a very recent study, involving the TiO_2 -assisted photodegradation of 2,4-dichlorophenol, a rate-enhancing influence of $[Cu^{2+}]$ was reported and attributed to the reduction of Cu^{2+} by the heterogeneous

surface photoproduct e^- , thus diminishing the extent of recombination of the h^+e^- pair and thus resulting in an enhancement of the rate of the reaction [15].

It has been proven that Cu^{2+} ions reduce the extent of hole–electron recombination by trapping the photogenerated electrons [16,17]:



The reduced forms, in turn, prevent the recombination by trapping holes;



If a small quantity of Cu^{2+} effectively prevents hole–electron recombination even in the oxygenated suspensions, either holes or electrons escaped from the recombination produce $\cdot OH$ radicals via the corresponding routes, re-

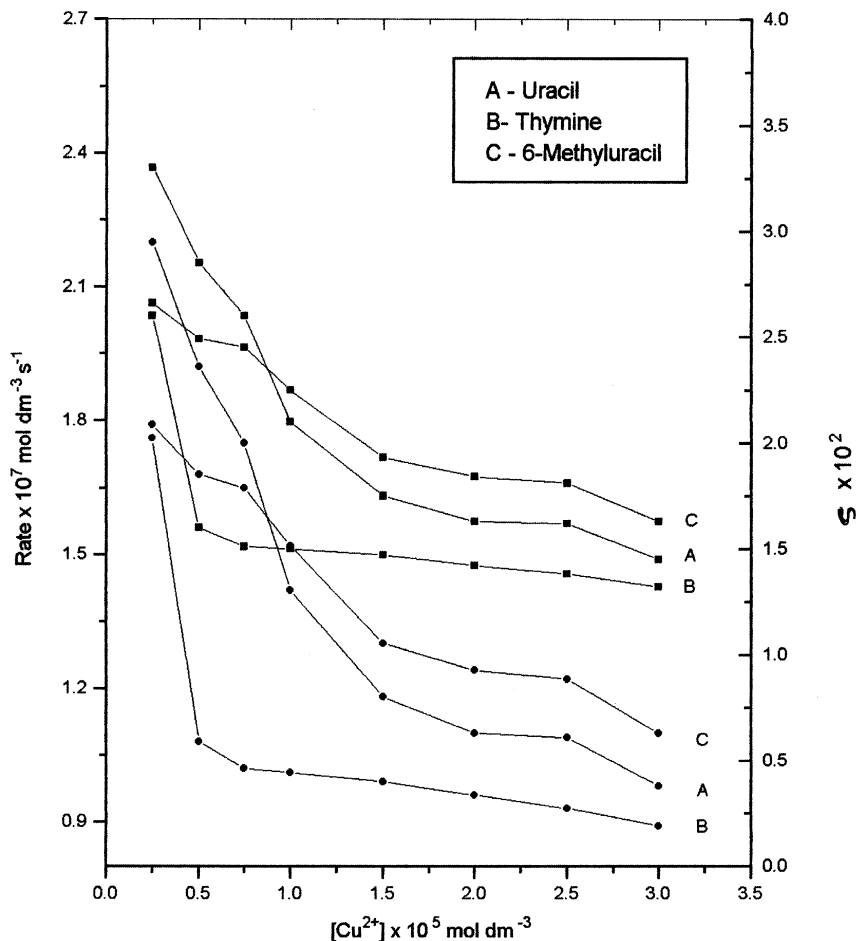


Fig. 1. Effect of $[Cu^{2+}]$: — — effect of $[Cu^{2+}]$ vs. rate, —■— effect of $[Cu^{2+}]$ vs. relative photonic efficiency (ζ).

sulting in the promotion of the reaction. Evidence for the involvement of Cu^+ was obtained in the present study from the agreement in the λ_{max} values of the UV spectrum of the irradiated solution when added to neocuproin and that of the one available from literature for the Cu^+ –neocuproin complex. Because Eqs. (1) and (2) are the short-circuiting reactions of Cu^{2+} [16,18], a large quantity of Cu^{2+} rather retards the reaction. The decrease in the rate of the photoprocess with increase in $[\text{Cu}^{2+}]$ is also due to the fact that the enhanced metal deposit (at higher Cu^{2+}) on the TiO_2 particle hinders the absorption of photons by the semiconductor [9], thus, leading to a decrease in the rate of electron–hole generation; hence, resulting in an

overall decrease of the reaction (heterogeneous photooxidation of the pyrimidine). It was observed that the diffuse reflectance spectrum of TiO_2 in Cu^{2+} exhibited a bathochromic shift (by about 20 nm) compared to the one in the absence of Cu^{2+} . This indicates that there is an adsorption of Cu^{2+} on TiO_2 , which, in a way, blocks the effective area of TiO_2 thus diminishing its capacity to absorb more light which finally leads to a decrease in the reaction rate.

5. Effect of heat treatment of TiO_2

The dependence of photocatalytic activity (= rate of photodegradation) on the calcination

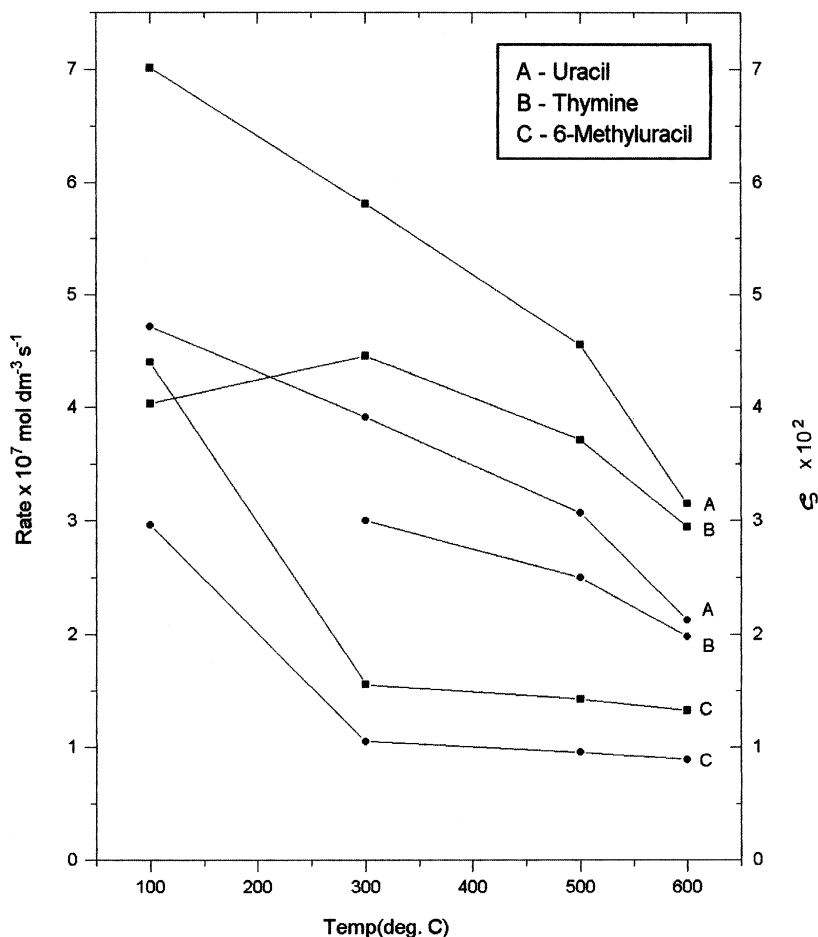


Fig. 2. Influence of heat treatment: - - - effect of temperature ($^{\circ}\text{C}$) vs. rate, —■— effect of temperature ($^{\circ}\text{C}$) vs. relative photonic efficiency (ζ).

temperature of TiO₂ was studied by preheating the TiO₂ powder (before irradiation) in the range of 200–600°C. For all the pyrimidines studied, it could be inferred (Fig. 2) that an increase in calcination temperature resulted in a decrease in the rate of the photocatalytic process. This could be attributed to the role of surface bound peroxy groups on TiO₂ [10]. It is clear that calcining at higher temperature drives away the surface-bound peroxy species (formed through coordinated OH groups). These surface peroxy species are proven to be electron traps [10]. Hence, due to the decreased amount of these peroxy species at higher calcination temperatures, the e⁻-h⁺ recombination becomes enhanced. Consequently, the efficient photogeneration of h⁺ and thus the attack of the pyrimidine molecules by h⁺ and ·OH radical (the latter being formed through h⁺ + OH⁻ → ·OH) are diminished, finally retarding the reaction rate. This effect of calcination temperature could also be due to the transformation of the active metastable anatase form to the stable rutile form, the latter being relatively an inactive one.

In order to assess the role of calcination temperature of TiO₂ on its UV absorption, the absorbance of a suspension of TiO₂ in a 1:1 mixture of water and polyethylene glycol was measured at 365 nm. It was noticed that the absorbance of the experimental solution decreased gradually with an increase in calcination temperature. Hence, it is clear that the particle calcined at lower temperature absorbs more UV radiation and the amount of absorption decreases with an increase in calcination temperature. This observation is due to the fact that surface area decreases with an increase in calcination temperature, thus effecting a corresponding decrease in the rate of photoprocess because of diminished rate of absorption of UV photons by TiO₂ at higher calcination temperatures [19]. Such a phenomenon has also been reported in an earlier study [19]. The product formed in the present work is the corresponding 5,6-dihydroxy-pyrimidine as has been confirmed in our earlier work and published [8].

6. Conclusions

(1) The quantum yield for TiO₂-mediated photooxidation of Uracil, thymine and 6-methyluracil has been expressed in terms of a suitably modified term, the “relative photonic efficiency (ζ)” considering the heterogeneous nature of the aqueous suspension.

(2) An unusual retarding role of added Cu²⁺ on ζ observed in this work has been explained on the basis of the short-circuiting redox behaviour of Cu²⁺ in the photoreaction.

(3) Experiments carried out with TiO₂ calcined at different temperatures revealed a decreasing trend in its photocatalytic activity attributable to the transformation of the active anatase form to the inactive rutile one of TiO₂ and also due to the decreased availability of effective e_{cb}⁻ capturing surface-bound peroxy species at higher temperatures.

Acknowledgements

R.R thanks the Department of Science and Technology, New Delhi, for financial support (SP/S1/F.12/'94). V.K.V thanks DST for a fellowship. M.R.D. thanks University Grants Commission New Delhi, for the award of senior research fellowship.

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