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Photocatalytic oxidative degradation of 2-methylthiophene In suspensions of TiO_2: identification of intermediates and degradation pathways

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Abstract

The photocatalytic oxidative degradation of 2-methylthiophene has been investigated in aqueous suspensions of TiO_2. The nature of the degradation products was investigated using GC/MS. The effects of the nature of the solvent and type of radiation have also been examined. In the degradation of 2-methylthiophene several intermediates were detected including hydroxythiophenes, various dimeric and trimeric structures. © 2001 Published by Elsevier Science B.V.

Keywords: Photodegradation; TiO_2; 2-Methylthiophene

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1. Introduction

Solar energy is a renewable energy form; cost effective, completely free, and which can be used directly to oxidise hazardous organic chemicals to carbon dioxide, water and simple mineral acids. Although a few compounds can undergo direct reactions when they are exposed to light, a wide range of other organic compounds can be destroyed in the photochemical processes [1]. Photocatalytic processes can take place either in a homogenous medium containing a suitable additive (e.g. hydrogen peroxide or ozone) or in a colloidal (heterogeneous) suspension of semiconductor particles, e.g. titanium dioxide [2].

Detailed applications of this photocatalytic process have been extensively reviewed by Goswami recently [3]. Heterogeneous photocatalysis is a process in which the illumination of an oxide semi-conductor, usually anatase or rutile, produces photo-excited electrons (e^-) and positive charged holes (h^+). The photo excitation of the semi-conductor particles by UV light changes the energy state of the electrons from the valence band of the solid to the conduction band and general equations for titanium dioxide in aqueous systems and the mechanism of the titanium dioxide photocatalysed oxidative degradation are described previously [4].

When titanium dioxide is irradiated by UV ($\lambda < 390\,\text{nm}$), it generates h^+_{VB}/e^-_{CB} pairs and these species migrate to the solid surface. The surface of the semi-conductor becomes so strongly oxidising that it can initiate the oxidation of organic pollutants at the solid–liquid surface in water by converting dissolved dioxygen, water or hydroxyl ions to hydroxyl radicals and other radicals, such as $O_2^{\bullet -}$ and $HO_2^{\bullet}$. The formation of hydroxyl radicals in aqueous titanium dioxide suspension was proved by EPR measurements [5]. Although there is supportive evidence about the formation of hydroxyl radicals, controversy still exists as to whether h^+_{VB} or $HO^{\bullet}$ radicals are responsible for the oxidation process as the dominant species. It is known that oxidation by holes occurs because trichloroacetic acid and oxalic acid were observed as intermediates during the oxidation of chlorinated ethanes in the presence of hydroxyl radicals (UV/titanium dioxide system) [6].

Early studies involved the use of a low pressure mercury lamp but recent modifications involve high intensity UV lamps which possess higher energy outputs and higher electrical efficiencies with a lower cost, broad band spectrum output and increased efficiency.

The effectiveness of the titanium-dioxide-assisted photodegradation process largely depends on the nature of the substrate. For example, while shorter illumination times are

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required (20–40 min) for the complete oxidation of coloured compounds, 24 h are required for chlorophenols. Also the formation of different intermediate products revealed differences between direct and titanium-dioxide-assisted photolysis. The rate of degradation is also influenced by several other factors, such as pH, titanium dioxide concentration, temperature, quantity of dissolved oxygen, light intensity and type, the presence of dissolved anions and cations and metal loading [7–9]. All studies, in particular, suggested that the optimum titanium dioxide concentration for oxidation is 2.0 g/l, since a higher titanium dioxide concentration could cause lower light penetration resulting in lower oxidation rates. The optimisation of all factors rigorously depends on the chemical character of the substrate.

A detailed literature search showed that the photocatalytic degradation of sulphur-containing heterocyclic compounds has not been studied. In consequence, we have decided to apply this technique to the model compound 2-methythiophene as representative of alkylthiophenes which occur in petroleum and cooking-plant wastes. The main purpose of this study is to determine the nature of the intermediate oxidation products and to establish possible reaction pathways. The photocatalytic oxidation of 2-methylthiophene was studied in aqueous solution and the reaction was conducted in the presence and absence of titanium dioxide under an oxygen atmosphere. Since 2-methylthiophene is not soluble in water, and solubility affects the oxidation rate, the photocatalysed oxidation was conducted using dichloromethane as a co-solvent system. For comparison, the reaction was also carried out solely in water, but with vigorous stirring.

2. Experimental

2.1. Photocatalytic oxidation reactions of 2-methylthiophene

Two different experiments were used for the photocatalytic oxidations of 2-methylthiophene in a quartz photoreactor fitted with low pressure mercury lamp; the first oxidation process was carried out in aqueous solution (no organic solvent) (100 cm^3) while the second involved the presence of dichloromethane/water (50 cm^3/50 cm^3). Each reaction was repeated with and without the presence of titanium dioxide and the reaction conditions are summarised in Table 1.

Table 1
Experimental conditions of photocatalytic oxidation of 2-methylthiophene (0.01 mol)

Catalyst	Solvent	Illumination
–	H_2O	Sunlight
TiO_2	H_2O	Sunlight
–	CH_2Cl_2/H_2O	Sunlight
TiO_2	CH_2Cl_2/H_2O	Sunlight
–	H_2O	Visible lamp light ($\lambda > 300$ nm)
TiO_2	H_2O	Visible lamp light
–	CH_2Cl_2/H_2O	Visible lamp light
TiO_2	CH_2Cl_2/H_2O	Visible lamp light
–	H_2O	Low pressure UV lamp ($\lambda = 254$ nm)
TiO_2	H_2O	Low pressure UV lamp
–	CH_2Cl_2/H_2O	Low pressure UV lamp
TiO_2	CH_2Cl_2/H_2O	Low pressure UV lamp

The requirement of a co-solvent system (dichloromethane/water) for the photocatalytic oxidation of 2-methylthiophene was shown by the preliminary results since no oxidation products were observed in the presence of titanium dioxide when the reaction was conducted in water only. Hsiao et al. showed [10] that titanium-dioxide-catalysed photooxidation of dichloromethane gave only hydrochloric acid and carbon dioxide over a 4 h illumination time with 320–400 nm light in a photoreactor. This result indicates that using dichloromethane does not interfere with the oxidation products generated from the photooxidation of 2-methylthiophene. Dissolving 2-methylthiophene in dichloromethane increases the possibility of contact of 2-methylthiophene with the surface of titanium dioxide with vigorous stirring.

The photocatalyst used in this study was titanium dioxide powder supplied by Aldrich. The particles are spherical and non-porous, primarily in the anatase structural form with greater than 99.9% purity. The primary particle size is 325 mesh with a specific BET surface area of 9.8 m^2/g. The 2-methylthiophene and dichloromethane used for the reaction were reagent grade purchased from Aldrich. The reactions were carried out in a quartz reactor. The reactor was cylindrical and ca. 200 cm^3 capacity equipped with a glass stirrer device and was cooled down to 40–45°C with the help of the water circling outside the reactor. 0.2 g titanium dioxide and 100 cm^3 double distilled water were added to the reactor vessel. After addition of 2-methylthiophene (1.02 g, 0.01 mol) which was previously dissolved in dichloromethane or water, the suspension was illuminated by an already warmed up low pressure mercury lamp (254 nm wavelength) and the reaction vessel was sealed. Other photooxidation reactions which require direct sunlight and lamplight were conducted in a three necked pyrex round bottomed flask with magnetic stirrer and a condenser. The temperature was kept at 40–45°C with a hot plate and the flask was then sealed. After the appropriate time period (from 1 to 3 h), the reaction mixture was extracted with dichloromethane (2×50 cm^3) or the dichloromethane phase was separated. After drying over $MgSO_4$, the organic layer was evaporated down to 2 cm^3 under reduced pressure and the resulting extract was analysed by GC/MS, the conditions, the instrument and the temperature program are described below.

2.2. Sample analysis

Dichloromethane extracts were analysed using a capillary column gas chromatograph coupled to a mass spectrometer. The instrument used was a VG Trio 1 Mass

Table 2
The products arising from the photolysis of 2-methylthiophene in the absence of titanium dioxide

Comp. No	t_R (min)	Apparent molecular mass	Solvent	Proposed structure
1	7.83	112	CH_2Cl_2/H_2O	Thiophene-2-aldehyde
2	23.57	194	CH_2Cl_2/H_2O	2-Methyl-5-(2-thienylmethyl)thiophene
3[a]	37.29	290	CH_2Cl_2/H_2O	Unknown trimeric structure

[a] Indicates that proposed structure has not been proved by comparison with the authentic substance.

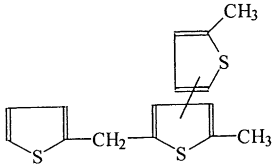
Quadrupole Spectrometer (Manchester, UK) coupled to a 5890 Hewlett-Packard Gas Chromatograph (Avondale, PA). The conditions used involved a ramp program (40 (5 min) to 250 (5 min) at 5°C min^{-1}) and due to the polarity of the system being used, an Econo-Cap Capillary SE-54 (30 m, immobilized 5% diphenyl, 95% dimethylpolysiloxane) column was used.

After detection on GC/MS either appropriate standard compounds were analysed under the same conditions or spiked into the reaction mixtures. Both retention times and mass spectral fragmentations of products were compared with those of the standards.

3. Results and discussion

All direct photolysis reactions of 2-methylthiophene in the dichloromethane/water system gave three main oxidation products in the absence of titanium dioxide. The reaction products are summarised in Table 2 and Scheme 1 represents the oxidation products observed. The structures were assigned by comparison with authentic samples or by consideration of mass spectral data.

Components (**1**) and (**2**) were confirmed by comparing with authentic samples. The structure of component (**3**) was suggested from the mass spectral fragmentation with an apparent molecular ion at *m/z* 290 and a stable ion at *m/z* 275 (M-15). This compound might be formed due to the addition of another thiophene ring to the component (**2**) since the molecular mass increase is 96 and showed the same mass spectral fragmentation as (**2**). This product was isolated from the reaction mixture as pure brown oil, whose structure has not been completely evaluated but a possible structure (**3**) is suggested from its mass spectral fragmentation and NMR spectrum.



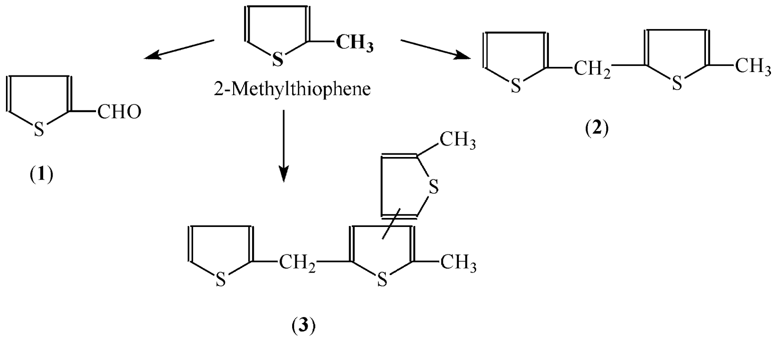
(**3**)

The breaking of bonds is a common photochemical process usually generating free radicals. Hydroxyl radicals ($HO^{\bullet}$) are assumed to be produced by photolysis of water ($\lambda < 200$ nm), leading to the formation of further free radical species [11,12]. These free radicals may lead to the compounds (**2**) and (**3**). Most probably the transformation of methyl thiophene under this conditions (in the absence of TiO_2, $\lambda > 200$ nm) is due to its direct photolysis and the formation of radicals may be attributed to an oxidative process. This possible pathway is shown in Scheme 2. Longer illumination time significantly increased the formation of component (**3**), resulting in approximately a 1% yield.

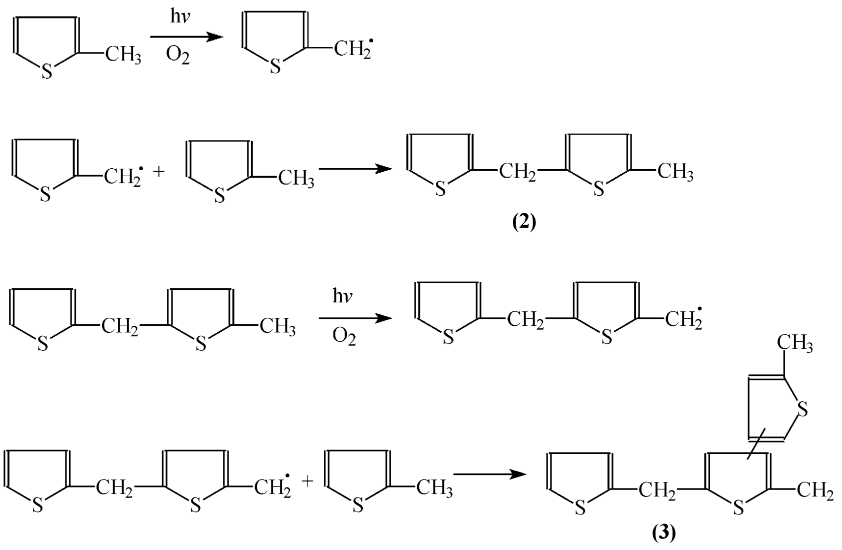
Photocatalytic oxidation of 2-methylthiophene in the presence of titanium dioxide gave the same products given above, together with other oxidation products. The reaction products are summarised in Table 3 and Scheme 3.

All these products were identified by comparing them with authentic samples. Similar products to those observed in the absence of titanium dioxide were formed, but using low pressure UV light shortened the reaction time giving oxidation products even after a 1 h illumination period.

A second interesting observation from this experiment is the formation of ring cleavage products, such as S_8 and



Scheme 1.



Scheme 2.

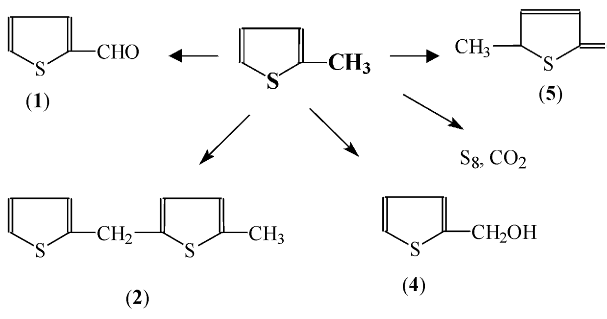
Table 3
The products arising from the photocatalysed oxidation of 2-methyl thiophene in the presence of TiO_2

Comp. No	t_R (min)	Apparent molecular mass	Solvent	Proposed structure
1	7.83	112	CH_2Cl_2/H_2O	Thiophene-2-aldehyde
2	23.57	194	CH_2Cl_2/H_2O	2-Methyl-5-(2-thienylmethyl)thiophene
4	9.85	114	CH_2Cl_2/H_2O	2-Hydroxymethylthiophene
5	10.15	114	CH_2Cl_2/H_2O	5-Methyl-(5H)thiophen-2-one

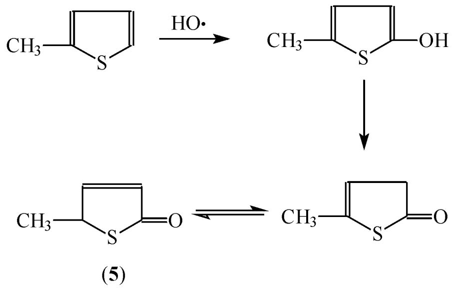
carbon dioxide. When the concentration of the unreacted 2-methylthiophene was monitored over a 3 h period, it showed a linear decrease with illumination time. Half of the initial 2-methylthiophene was oxidised or decomposed during the photocatalytic treatment over a 3 h period. The formation of the hydroxylated intermediates 2-hydroxymethylthiophene (**4**) and 5-methyl-(5H)thiophen-2-one (**5**) indicates the involvement of hydroxyl radical, following work by Goldstein et al. [13] (Scheme 4). The formation of the ketonic derivative was experimentally proven [14,15].

However, the above titanium-dioxide-assisted photocatalytic oxidation of 2-methylthiophene does not seem to be very effective for the complete destruction of this substrate (only 50% decomposed or oxidised). On the other hand, the concentration used (0.01 mol) is not consistent with usual environmental conditions and the formation of oligomers is probably favoured by this relatively high concentration. But the process may be developed, especially for the treatment of more dilute solutions (e.g. 10^{-5}–10^{-6} mol dm^3) perhaps involving longer illumination periods resulting the hydroxylated thiophene and ring cleavage products.

Although the oxidation rates are slow, oxidative degradation of 2-methylthiophene with TiO_2/UV was successfully achieved and intermediate products have been characterised. The formation of dimeric and trimeric structures suggests that the products observed might be formed via a radical route. The photooxidation process is a developing new technique but it seems to be ineffective for complete oxidative



Scheme 3.



Scheme 4.

conversion of the relatively concentrated solutions studied. However, further improvements may provide greater efficiency especially for dilute solutions. New process designs and the further developments of photochemical technologies will be significant steps forward for this environmentally friendly cleaning up process.

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