ELSEVIER
Journal of Photochemistry and Photobiology A: Chemistry 155 (2003) 199–205
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photodecomposition of ozone sensitised by a film of titanium dioxide on glass

Andrew Mills*, Soo-Keun Lee, Anne Lepre

Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK

Received 10 June 2002; received in revised form 1 October 2002; accepted 18 October 2002

Abstract

High levels of ozone (typically 850 ppm) are readily decomposed by semiconductor photocatalysis, using a thin film of the semiconductor titanium dioxide (Degussa P25 TiO_2) cast on a glass tube, and UVA light, i.e. light of energy greater than that of the bandgap of the semiconductor (ultra-bandgap light); in the absence of this light the thermal decomposition of ozone is relatively slow. The semiconductor films show no evidence of chemical or photochemical wear with repeated use. At high levels of ozone, i.e. $100\,\text{ppm} \leq [O_3] \leq 1400\,\text{ppm}$, the initial rate of ozone decomposition by semiconductor photocatalysis is independent of $[O_3]$, whereas, at lower ozone concentrations, i.e. $5\,\text{ppm} \leq [O_3] \leq 100\,\text{ppm}$, the initial rate of ozone photodestruction decreases in a smooth, but non-linear, manner with decreasing $[O_3]$. The kinetics of ozone photodecomposition fit a Langmuir–Hinshelwood type kinetic equation and the possible mechanistic implications of these results are briefly discussed.

Keywords: Ozone; Photocatalysis; Semiconductor; Photodecomposition; Titanium dioxide

1. Introduction

Ozone, the triatomic form of oxygen, i.e. O_3, is a powerful oxidant and very reactive gas. As a consequence of its high reactivity, ozone is a very toxic material and the recommended threshold level for allowable exposure during an 8 h period is very low, i.e. 0.1 ppm [1]. Ozone causes headaches, throat dryness and damage to mucous membranes at levels as low as 0.1–1 ppm and can be life-threatening a levels higher than this. Given its high toxicity it is surprising, therefore, to note that sources of ozone are commonplace in the work environment. For example, cooling air from photocopies and laser printers carry large amounts of ozone generated by the corona discharge process and, as a result, the fan-extracted air is usually treated using an activated carbon filter, before being released. Ozone is also used extensively in industry for sterilization, waste water treatment and the bleaching of cloth and wood pulp [2]. In all such applications, any effluent must have its level of ozone reduced before being released into the environment. Thus, possibly of more concern is the popular use of ozone as a deodouriser in places in which direct exposure to humans is inevitable, such as in public washrooms and hotel rooms contaminated with cigarette smoke. It is not surprising, therefore, that there is a great deal of interest in methods for decomposing ozone to harmless products.

Although the decomposition of ozone is a thermodynamically favoured process, i.e.

$$2O_3 \underset{\Delta G=-163\,\text{kJ}\,\text{mol}^{-1}}{\rightarrow} 3O_2 \tag{1}$$

ozone is thermally stable up to 523 K and, as a consequence, will stay in the environment until it reacts oxidatively unless treated [3]. One method of treatment is the use of activated carbon filters, but these cannot be regenerated and require frequent replacement and subsequent disposal. Another method of treatment is irradiation of ozone with UVC light, i.e. $280\,\text{nm} \leq \lambda$, since it is prone to photochemical decomposition, i.e. photolysis [4,5]. Indeed, the quantum yield for this process extrapolated to zero ozone pressure is ca. 4 [4]. However, this treatment method is not usually very effective since ozone only absorbs weakly in this region, i.e. $\varepsilon_{254} = 130\,\text{atm}^{-1}\,\text{cm}^{-1}$, [4,5]. Another major method of treating ozone is the use of catalysts for mediating its decomposition, i.e. reaction (1) [1]. The most popular catalyst for this purpose is manganese (IV) oxide, MnO_2, on a high surface area support, such as γ-alumina or titanium (IV) oxide, TiO_2 [6,7]. MnO_2 appears highly active and robust as a catalyst for reaction (1) and, as a result, forms the basis of many patents [1]. Not surprisingly, work shows that the support material,

---

* Corresponding author.
E-mail address: a.mills@strath.ac.uk (A. Mills).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00388-X

such as TiO_2, exhibits little or no catalytic activity when compared to the active catalyst deposited on its surface [1].

Early work carried out by others established that reaction (1) can also be mediated by semiconductor photocatalysis using TiO_2 [8–10]. In semiconductor photocatalysis, ultra-bandgap illumination of the semiconductor generates an electron-hole pair, i.e. reaction (2); the photogenerated electron and hole are then able to oxidize suitably reactive species on the surface of the semiconductor photocatalyst. In the photocatalytic decomposition of ozone, it appears likely that the photogenerated electron reduces surface adsorbed ozone to form the highly unstable and reactive species, ${O_3}^-$, i.e. reaction (3) [8]. The photogenerated hole is likely to react with a surface hydroxyl group to form a hydroxyl radical, reaction (4). The ${O_3}^-$ ion can be oxidized to ${O_4}^-$ by ozone, i.e. reaction (5), and the hydroxyl radical can react with ozone to form another unstable species, ${O_4}^-$, i.e. reaction (6). Evidence for this sequence of events, and the two highly unstable reaction intermediates ${O_3}^-$ and ${O_4}^-$, comes primarily from the work of Gonzalez-Elipe and Soria in their epr study of the various species generated on the surface of hydrated, dehydrated and chlorinated anatase TiO_2 upon exposure to ozone and UV irradiation at 77 K [8]. Although Gonzalez-Elipe and Soria found that the overall process at 77 K leads to the formation of ${O_4}^-$ and H_2O_2 (generated via an ${O_3}^-$ disproportionation reaction), ${O_4}^-$ is not stable at room temperature and UV irradiation of TiO_2 does not lead to the generation of significant amounts of hydrogen peroxide [8,11]. Thus, the product of ozone photocatalytic destruction, sensitised by TiO_2 at room temperature is simply oxygen. Given its reactivity and instability, there are many possible fates for ${O_4}^-$ at room temperature, but its reaction with either ozone, i.e. reaction (7), or with ${O_3}^-$, i.e. reaction (8), appear the most likely. Thus, at room temperature, the photodecomposition of ozone, sensitized by TiO_2, may follow the overall reaction scheme as proposed by Gonzalez-Elipe and Soria [8] but with some slight modification, such as the introduction of reactions (7) and (8) so that the final product is oxygen. The proposed modified reaction scheme is as follows:

$$TiO_2 \xrightarrow{h\nu \geq 3.2\,\mathrm{eV}} h^+ + e^- \tag{2}$$

$$e^- + O_3 \rightarrow {O_3}^- \tag{3}$$

$$h^+ + OH^- \rightarrow OH^\bullet \tag{4}$$

$$ {O_3}^- + O_3 \rightarrow {O_4}^- + O_2 \tag{5}$$

$$OH^\bullet + O_3 \rightarrow {O_4}^- + H^+ \tag{6}$$

$$ {O_4}^- + O_3 \rightarrow 2O_2 + {O_3}^- \tag{7}$$

$$H^+ + {O_3}^- + {O_4}^- \rightarrow 3O_2 + OH^- \tag{8}$$

where the overall process can be summarized as:

$$2O_3 \xrightarrow[TiO_2]{h\nu \geq 3.2\,\mathrm{eV}} 3O_2 \tag{9}$$

Ohtani et al. studied the catalytic and photocatalytic activity of TiO_2 for ozone decomposition, using a wide range of photocatalysts derived from a number of different sources [9]. The photocatalytic activity was found to be independent of specific surface area but dependent upon crystal structure, increasing in the order anatase $\ll$ anatase-rutile mixture $<$ rutile. Other research carried out by these workers showed that Ag, deposited onto the surface of TiO_2, enhanced the overall photocatalytic activity for ozone destruction via reaction (9) for most samples of TiO_2 tested [10].

The work described in this paper builds on the primary studies conducted by others outlined above. In particular, this paper describes the results of a study of the kinetics of reaction (9) photosensitized by films of titanium dioxide cast on a glass substrate.

2. Experimental

2.1. Materials

The TiO_2 films on glass substrates used in this study were prepared using Degussa P25 TiO_2 powder in a procedure described previously in detail elsewhere [12]. Briefly, the films were cast by dipping cylindrical glass tubes, ca. 8 × 1.7 cm (o.d.), into a 5 wt.% per volume aqueous slurry of Degussa P25 TiO_2, washing with distilled water and drying, first in an air stream and then in an oven at 80 °C for 1 h. This process was repeated three times for each tube to yield a 'three-coat' film that was then used without further treatment. Films produced by this method are stable to repeated washing with water but are not stable to mechanical abrasion. Previous work established that a three-coat film has a density of $0.102\,\mathrm{mg\,cm^{-2}}$ [12]. Profilometry revealed that the films had a typical thickness of 0.58 μm. The UV-Vis spectrum of a three-coat film of Degussa P25 on glass is illustrated in Fig. 1 and shows the film to be highly scattering at sub-bandgap wavelengths, such as 400 nm, but also strongly absorbing at ultra-bandgap wavelengths, such as 380 nm.

Ozone was generated using an ozone generator (Peak Scientific Instruments Ltd., UK, model OZ06), supplied with a constant feed of oxygen (BOC Ltd., UK) from a cylinder. In this instrument, the ozone is generated by corona discharge using a high frequency, high voltage power supply to convert oxygen in the feed gas into ozone.

3. Methods

At high levels of ozone (100–1400 ppm), the thermal and photocatalytic decomposition of ozone were monitored spectrophotometrically at 254 nm (molar absorptivity $1.3 \times 10^{-4}\,\mathrm{ppm^{-1}\,cm^{-1}}$ [5]) at room temperature (293–298 K) using 10 cm cylindrical Pyrex spectrophotometer gas cell, 2.2 cm (o.d.), fitted with detachable quartz windows at each

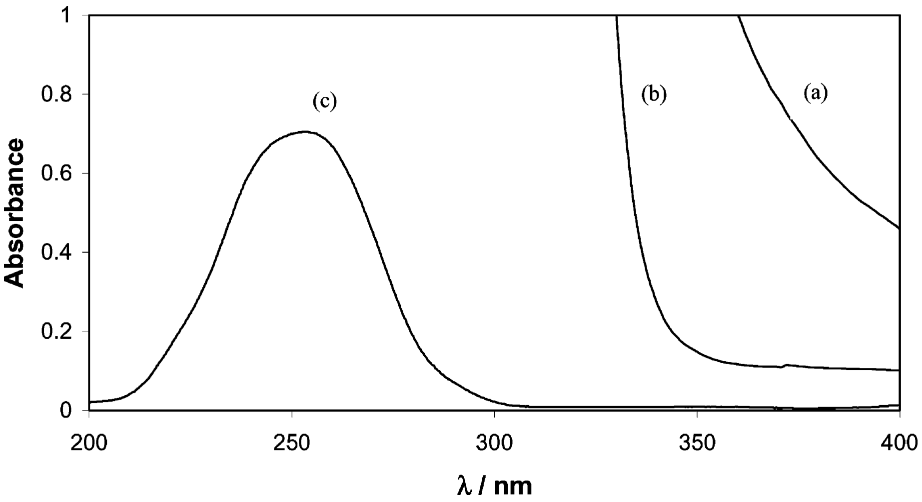

Fig. 1. UV-Vis spectra of (from right to left) (a) a three-coat TiO_2 film on glass, (b) a 1 mol dm^{-3} potassium nitrate filter and (c) 580 ppm of gaseous ozone in an 10 cm spectrophotometer cell.

end, through which an 8 cm (1.7 cm o.d.) P25 TiO_2-coated cylindrical inner tube was inserted. The cell also had a gas inlet and outlet tap to allow it to be filled to the desired level of ozone from the ozone generator before being sealed off by closing both taps. The cell was placed in a UV-Vis spectrophotometer (Perkin–Elmer, Lambda 3) to allow the absorbance of the cell at 254 nm to be monitored continually throughout each experiment. The UV-Vis absorption spectrum of 580 ppm of ozone was recorded using this cell/spectrophotometer configuration and is illustrated in Fig. 1. The absorption band appears broad and featureless with a maximum at ca. 254 nm.

Ultra-bandgap illumination was derived from an external light source arranged perpendicular to the 10 cm spectrophotometer gas cell and monitoring beam of the spectrophotometer. The light source was an Xe–Hg arc lamp, heavily filtered using a water filter, to prevent heating of the cell, and a 1 mol dm^{-3} potassium nitrate filter, to ensure that only light of greater than 340 nm was transmitted. The potassium nitrate filter was necessary to prevent direct, i.e. photolytic [4], rather than photocatalytic, photodestruction of ozone by short wavelength UV light. The UV-Vis spectrum of the potassium nitrate filter is illustrated in Fig. 1. The light output from the illumination source was quantified by ferrioxalate actinometry [13]. When the cell was irradiated with ultra-bandgap light (365 ± 25 nm) the photodetector of the spectrophotometer was protected from over-saturation by scattered stray UV light by blocking the transmitted light inlet port with a piece of black card. Thus, in this system, no absorbance measurements and, therefore no ozone measurements, were made during the process of exposing the sample under test to ultra-bandgap irradiation, rather [O_3] measurements were made in-between such irradiations.

The kinetics of photocatalytic destruction of low levels of ozone (120 ppm–5 ppm) were also monitored spectrophotometrically, but this time using a reaction cell with a much longer pathlength, i.e. 100 cm, and an inner glass tube, 99 × 1.7 cm (o.d.), uncoated or coated with TiO_2. The 1 m glass tube reaction cell was mounted on an optical bench and the absorbance monitored using, at one end, a deuterium light source, filtered so as to allow only the UV component to be transmitted, as the monitoring light source and, at the other end, a monochromator (set at 254 ± 20 nm) and photomultiplier (Applied Photophysics, London, UK) as the transmitted light intensity detection system. In this work, ultra-bandgap illumination of the TiO_2 film on the inner glass tube was provided by two half-cylinders, each containing six 8 W Coast-Wave Blacklight UVA lamps, arranged along the length of the1m reaction cell.

4. Results and discussion

4.1. Initial results at high ozone concentration

In order to establish the efficacy of TiO_2 as a photocatalyst for the decomposition of ozone, an initial high level of ozone (ca. 1100 ppm) was introduced into the 10 cm cylindrical spectrophotometer cell (2.2 cm o.d.), containing an 8 cm glass tube (1.7 cm o.d.) coated with three coats of Degussa P25, as described in Section 3. The ozone-containing system was then sealed, the cell placed in the UV-Vis spectrophotometer and the absorbance due to the ozone gas in the cell monitored at 254 nm. At specific time intervals the cell and its contents were subjected to a brief (30 s) exposure of ultra-bandgap irradiation from the filtered output of an Xe–Hg lamp placed perpendicular to the sample cell. As noted in Section 2, it was necessary to protect the photodetector of the spectrophotometer during the irradiation periods and, as a consequence, there were breaks in the recorded absorbance (due to ozone) versus time profiles arising from this work.

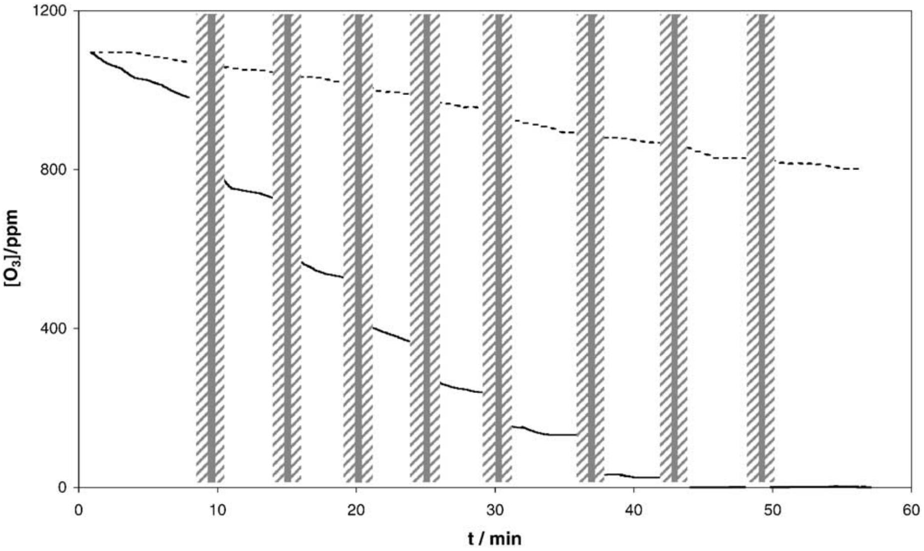

Fig. 2. Ozone concentration versus time profiles recorded in an 10 cm spectrophotometer cell, containing a glass tube (1.7 cm (o.d.) × 8 cm) with (solid line) and without (dashed line) a three-coat film of TiO_2. The hatched gray vertical lines indicate the time regions when no absorbance measurements were made because the sample under test was being exposed to ultra-bandgap light from an Xe–Hg lamp and, as a consequence, the spectrophotometer had to be blanked off. The solid gray vertical lines in the middle of the gray hatching represent the actual times (30 s) the sample was exposed to the ultra-bandgap light.

The typical ozone concentration versus time profiles for a glass tube with and without a film of TiO_2 are illustrated in Fig. 2. From the results of this work, for the uncoated glass tube, i.e. no TiO_2 present, it appears that ozone decomposes slowly with time in the absence of UV light and this is probably due to its slow reaction with the small number of oxidisable organic components of the cell, such as the PTFE taps and seals. The results for this tube also show quite clearly that the ozone gas is not photolysed by the ultra-bandgap light used in this work. This finding is as expected, since, as illustrated in Fig. 1, the UV-Vis absorption spectrum of ozone peaks at 254 nm and does not extend out much above 300 nm, whereas the ultra-bandgap light from the Xe–Hg lamp, that impinges on the ozone-containing reaction cell, is heavily filtered, using a strong potassium nitrate solution, and so contains little light of $\lambda \leq 340$ nm.

As illustrated in Fig. 2, the ozone concentration versus time profile for the glass tube with a three-coat TiO_2 film is markedly different from that for the uncoated film. Thus, in the absence of ultra-bandgap light, the absorbance due to ozone decreases at an enhanced rate for a TiO_2-coated glass tube compared to an uncoated glass tube, indicating that Degussa P25 TiO_2 is able to mediate to some extent the thermal decomposition of ozone, i.e. reaction (1). This finding gains support from the work of Ohtani et al. that notes that some samples of TiO_2 appear to show some catalytic activity towards the decomposition of ozone, as well as photocatalytic activity [9]. From the latter work, it appears that specific catalytic activity of TiO_2 increases with increasing degree of hydroxylation and specific surface area, suggesting that on TiO_2, at least, hydroxyls act as active sites for O_3 decomposition [9]. On this basis, it is not too surprising that the three-coat TiO_2 film exhibits some catalytic activity, since Degussa P25 TiO_2 is both a high surface area (typically 50 $m^2\,g^{-1}$) and highly hydroxylated material [14]. However, in comparison to more traditional catalysts for this process, such as MnO_2, TiO_2 is a relatively inactive material.

Most striking about the results illustrated in Fig. 2 is the sharp and almost constant drop, ca. 100 ppm, in $[O_3]$ produced upon irradiation of the TiO_2-coated glass tube with each 30 s exposure to ultra-bandgap, UV light. This result indicates that the photocatalytic decomposition of ozone, sensitised by TiO_2, i.e. reaction (9), is extremely efficient and can be rapidly and easily effected using UV light. This and other work showed that prolonged irradiation leads to the complete removal of ozone. The enthalpy change for reaction (1) (-143 kJ mol^{-1}) is large and exothermic. However, it appears unlikely that the surface temperature of the photocatalyst was raised sufficiently to drive the thermal decomposition of ozone any faster. An excellent indication of this is the apparent constant rate of the slow thermal decomposition of ozone before and after irradiation, as illustrated in Fig. 2.

In order for the TiO_2 film to be an effective photocatalyst for ozone decomposition it should ideally be able to work with repeated use without incurring any loss in activity due to chemical or photochemical wear. Thus, the effect of repeated use on the photocatalytic activity of a TiO_2 on glass film upon reaction (9) was tested by the repeated measurement of the degree of ozone destruction produced by a TiO_2-coated and uncoated glass tube upon its exposure to an ozone level of ca. 850 ppm and its subsequent irradiation with a 2 min burst of light from the filtered Xe–Hg lamp. Between each refill and irradiation the reaction cell

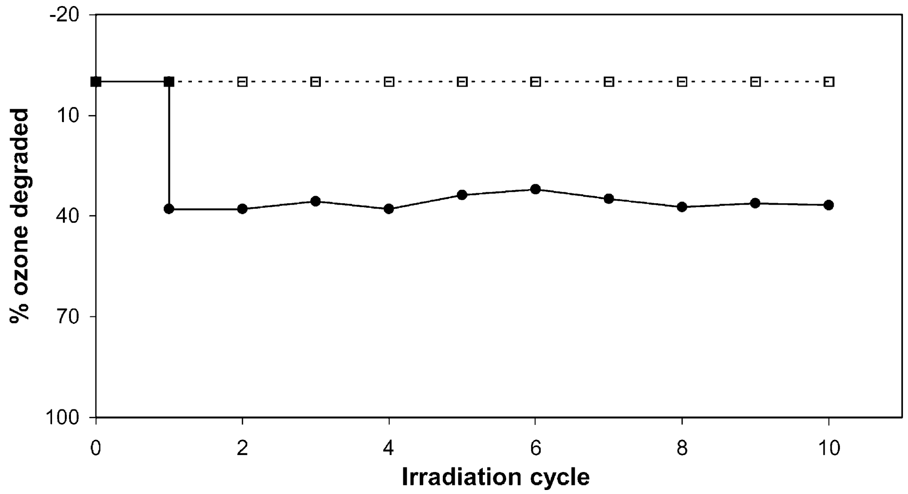

Fig. 3. Plot of the measured degree of ozone degradation as a function of irradiation cycle. In each irradiation 'cycle', the 10 cm spectrophotometer cell, containing the same 8 cm glass tube with (solid line) or without (dashed line) a three-coat film of TiO_2, was filled with the same level of ozone gas (850 ppm) of ozone, irradiated for 2 min with ultra-bandgap light, and the degree of ozone photodegradation produced was then measured.

was thoroughly flushed with oxygen to remove any unreacted ozone and reaction products. The results of this work are illustrated in Fig. 3 and show that in the absence of TiO_2 there is no measurable change in the ozone level with initial and repeated irradiation. In contrast, with TiO_2 present the level of ozone is consistently reduced to 40% of its initial value with each 2 min burst of ultra-bandgap irradiation. From these results it appears that the ability of the TiO_2 film to photosensitise the decomposition of ozone, i.e. reaction (9), is unaltered for a sequence of ten fills of ozone and its subsequent irradiation with ultra-bandgap light; the TiO_2 photocatalyst shows no evidence of any chemical, or UV light-induced, passivation or wear brought about by reaction (9) with repeated use.

The kinetics of ozone photodestruction, sensitized by the TiO_2 on glass films were studied by attempting to measure the initial rate of reaction (9), R_i, as a function of initial ozone concentration over the high initial ozone concentration range 100–1300 ppm. In this work, for reasons identified earlier, the $[O_3]$ versus time plots were all of the sort illustrated in Fig. 2 using heavily filtered light from an Xe–Hg lamp to ensure a less than 10% step change in the initial $[O_3]$ occurred with each burst of irradiation. Thus, from each such plot associated with a particular initial $[O_3]$ the initial rate was calculated as the ratio of the initial change in ozone concentration, $\Delta[O_3]$, to the irradiation time, Δt, i.e. $R_i = \Delta[O_3]\,\Delta t^{-1}$, where Δt was usually 30 s. From the results of this work, the kinetics appeared zero order with respect to $[O_3]$ and yielded an average initial rate of 1.7 ppm s^{-1}. Chemical actinometry provided a measure of the total number of photons of wavelength $<400\,nm\,cm^{-2}$ incident upon the TiO_2 film and allowed the calculation of a value of 0.011 for the formal quantum efficiency of the system, δ, where formal quantum efficiency is defined as [15,16]

$$\delta = \frac{\text{rate of photoreaction (units : molecules s}^{-1})}{\text{incident light intensity (units : photons s}^{-1})} \qquad (10)$$

For any photochemical process, the formal quantum efficiency is, by definition, ≤quantum yield [15]. Thus, the value of 0.011 quoted for δ for reaction (9) very much represents a minimum value for the quantum yield for the process. The latter parameter is usually very difficult to measure for a heterogeneous photochemical system, especially if it is highly scattering of the incident irradiation. Photocatalytic systems involving P25 TiO_2 as the photocatalyst invariably fall into this category since, although the fundamental particle size is ca. 21 nm, the aggregate powder particle size is 0.1 μm and, as a consequence, powder dispersions and cast films of P25 TiO_2 are usually highly scattering of sub-bandgap and weakly absorbed ultra-bandgap light. Indeed, in some cases, over 70% of the incident light can be lost due scattering and reflection [15]. As a consequence, in the study of such heterogeneous photocatalytic systems, formal quantum efficiencies provide rough, but useful measures of the photon to chemical conversion efficiencies of the systems and, by so doing, allows a limited, but useful, degree of comparison between such systems to be made. Thus, the value of 0.011 for δ for reaction (9) is not too dissimilar to that reported for the photodestruction of 4-chlorophenol in aqueous solution using a similar P25 TiO_2 film on glass as the photocatalyst ($\delta = 0.011$) [17].

4.2. *Kinetic study at low initial ozone concentrations (5–118 ppm)*

Although the kinetics of reaction (9) appear zero order at high (>100 ppm) levels of ozone, this may not be the case

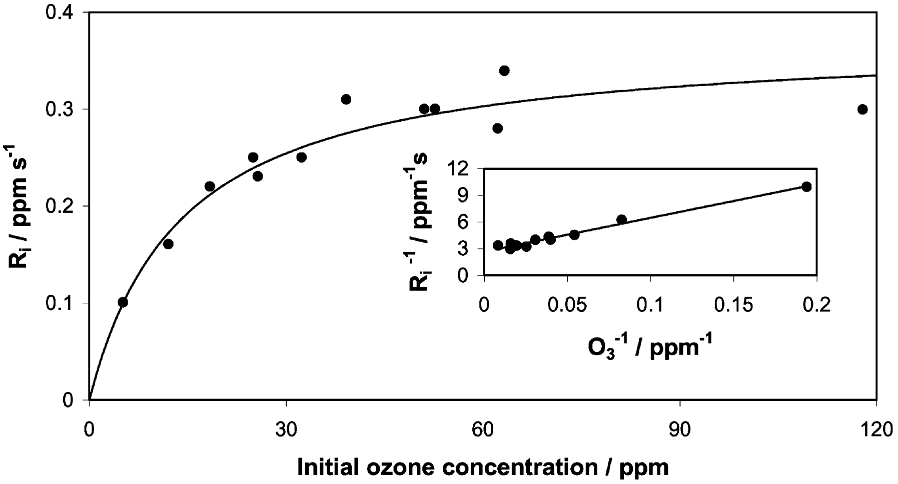

Fig. 4. Plot of the measured initial rate of ozone destruction, R_i, as a function of the initial concentration of ozone, [O_3]. The reaction cell was a 1 m cylindrical (2.2 cm o.d.) spectrophotometer cell, containing a 90 cm glass tube, 1.7 cm (o.d.), coated with three coats of TiO_2 and, filled with the desired initial level of ozone. The source of ultra-bandgap light were two half-cylinders laid along the length of the 1m spectrophotometer cell, each containing six 8 W (UVA) BLB bulbs. The insert diagram is a double reciprocal plot of the data in the main diagram and for which a line of best fit analysis reveals a gradient (k/K_{O_3}) and intercept (1/k) of 37.9 s and 2.68 ppm^{-1} s, respectively.

at lower levels. In order to monitor spectrophotometrically [O_3] at levels <100 ppm, a longer pathlength cell is required. Thus, in this work, a 1m reaction cell, containing a cylindrical, 99 × 1.7 cm (o.d.), uncoated or TiO_2-coated inner glass tube was employed as the photoreactor, along with an absorbance measuring system comprising a UV light source at one end and a monochromator and photomultiplier at the other, as described in Section 3.

Using this monitoring system, coupled with two half-cylinder irradiation units, each containing six 8 W BLB lamps, arranged in series along the length of the 1 m reaction cell, the initial rate of ozone photodestruction, R_i, was measured as a function of the initial ozone concentration over the range 5–118 ppm and the results of this work are illustrated in Fig. 4. These results show that R_i increases with increasing ozone concentration upto ca. 120 ppm, after which it levels out. The latter results are consistent with those reported earlier in this paper for high ozone levels.

The kinetics of many semiconductor sensitized photocatalytic reactions involving a substrate, S, are found to fit a Langmuir–Hinshelwood type kinetic equation [15], i.e.

$$R_i = \frac{kK_S(\text{substrate})}{1 + K_S(\text{substrate})} \qquad (11)$$

where k is a constant that is light intensity dependent (and may depend upon other parameters, such as [O_2] when S is an organic pollutant) and K_S is a constant that is usually found not to be simply the Langmuir dark adsorption coefficient for S adsorbed onto the semiconductor photocatalyst, i.e. $K_{L,S}$, and, indeed, may be also a function of light intensity [17,18].

If the kinetics of reaction (9) also fit a Langmuir–Hinshelwood expression, then from Eq. (11), a double reciprocal plot of the kinetic data illustrated in Fig. 4, i.e. 1/R_i versus 1/[O_3], should yield a straight line of gradient, $m = k/K_{O_3}$ and intercept, $c = 1/k$. This latter plot is illustrated in the insert diagram in Fig. 4 and, as predicted by Eq. (11), reveals a good straight line. The values of the gradient and intercept of this latter straight line plot allow the following values for k and K_{O_3} of 0.37 ppm s^{-1} and 0.071 ppm^{-1}, respectively, to be calculated. It is not clear if the value for K_{O_3} is the Langmuir dark adsorption coefficient for ozone on P25, i.e. K_{L,O_3}. If the value of K_{O_3} is that for K_{L,O_3}, then the observed kinetics for the decomposition of ozone can be readily interpreted in terms of the previously proposed reaction sequence (2)–(8) with reaction (3) as the rate-determining step and ozone adsorption fitting the Langmuir adsorption isotherm. However, semiconductor photocatalysis is often much more complicated than this, despite its tendency to exhibit simple Langmuir–Hinshelwood type kinetics that are easily fitted to simple, but inappropriate, kinetic models [19]. Thus, further work is required before a full understanding of the mechanism of ozone decomposition, sensitized by TiO_2 photocatalysis, can be gained.

5. Conclusions

Titanium dioxide films supported on glass are effective photocatalysts for the destruction of gaseous ozone with light of $\lambda > 340$ nm and can be used repeatedly over many cycles of ozone degradation without any appreciable loss in photocatalytic activity. At high ozone concentrations (>ca. 120 ppm) the photodegradation reaction is zero order with respect to [O_3]. At lower ozone concentrations, i.e. < 120 ppm, the kinetics are described very well by a Langmuir–Hinshelwood type kinetic equation. This latter finding could indicate that ozone adsorption on TiO_2 fits a

Langmuir adsorption isotherm and that the rate determining step is the initial reduction of an adsorbed ozone molecule by a photogenerated electron at the surface of TiO_2. However, for the moment, the proposed mechanism remains tentative and further work is required.

References

[1] B. Dhandapani, S.T. Oyama, Appl. Catal. B: Environ. 11 (1977) 129, and references therein.

[2] M.V. Byrd, K.J. Knoernschild, Tappi J. 75 (1992) 101.

[3] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Wiley-Interscience, New York, 1972, p. 410.

[4] I.T.N. Jones, R.P. Wayne, Proc. R. Soc. Lond. 319 (1970) 273.

[5] K.A. Rehme, in: R.G. Rice, M.E. Browning (Eds.), Ozone: Analytical Aspects and Odour Control, International Ozone Institute Inc., Jamesville, 1976, p. 17.

[6] W. Li, G.V. Gibbs, S.T. Oyama, J. Am. Chem. Soc. 120 (1998) 9041.

[7] W. Li, S.T. Oyama, J. Am. Chem. Soc. 120 (1998) 9047.

[8] A.R. Gonzalez-Elipe, J. Soria, Z. Phys. Chem. N.F. 126 (1981) 251.

[9] B. Ohtani, S.-W. Zhang, S. Nishimoto, T. Kagiya, J. Chem. Soc. Faraday Trans. 88 (1992) 1049.

[10] B. Ohtani, S.-W. Zhang, T. Ogita, S. Nishimoto, T. Kagiya, J. Photochem. Photobiol. A: Chem. 71 (1993) 195.

[11] A.H. Boonstra, C.A.H.A. Mutsaers, J. Phys. Chem. 79 (1975) 1940.

[12] A. Mills, J. Wang, J. Photochem. Photobiol. A: Chem. 118 (1998) 53.

[13] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1967, p. 783.

[14] G. Munuera, A.R. Gonzalez-Elipe, J. Soria, J. Sanz, J. Chem. Soc., Faraday Trans. 1 76 (1980) 1535.

[15] A. Mills, S. LeHunte, J. Photochem. Photobiol. A: Chem. 108 (1997) 1.

[16] T. Watanabe, T. Takizawa, K. Honad, J. Phys. Chem. 81 (1977) 1845.

[17] A. Mills, S. Morris, J. Photochem. Photobiol. A: Chem. 71 (1993) 75.

[18] A. Mills, J. Wang, Z. Phys. Chem. 213 (1999) 49.

[19] C.S. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178.