

The photochemical behavior of hydrogen peroxide in near UV-irradiated aqueous TiO₂ suspensions

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Abstract

The kinetic behavior of H₂O₂ decomposition in near UV-irradiated aqueous TiO₂ suspensions was investigated. The effects of the H₂O₂ concentration, the catalyst loading, the dissolved oxygen concentration, and the light intensity on the initial photodecomposition rate were studied. The observed kinetics were treated by both the Langmuir–Hinshelwood and the Freundlich model; the latter proved more successful for characterization of the system. The H₂O₂ photodegradation rate was found to be directly proportional to the light intensity and it increased with the catalyst concentration up to a saturation limit. The concentration of dissolved oxygen had no significant effect on the photodecomposition rate. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the end of the 1920s, the photochemical properties of H₂O₂ have been intensively investigated [1–3]. During recent decades, the number of publications has provided evidence of the continuing interest in the photochemical reactions of H₂O₂. Since the beginning of the 1990s, the semiconductor-mediated heterogeneous photocatalytic processes have become the most favored advanced oxidation processes, because of their promising applicability in water treatment and solar energy utilization. Many of these processes apply the TiO₂ as photocatalyst because of its favorable properties: non-photo-

corrosive, non-toxic, and capable of the photo-oxidative destruction of most organic pollutants.

Only some papers report on an accumulation of H₂O₂, generally in a very low concentration ($c \leq \mu\text{M}$), when irradiated TiO₂ is used as catalyst [4–8]. There can be two possible reasons for the only occasional detection of H₂O₂ formation in these systems: either its formation is very sensitive to the reaction conditions or its decomposition is very rapid, and it can therefore not accumulate in the solution. On the other hand, an increasing number of publications deal with the addition of H₂O₂ to irradiated semiconductor suspensions in order to attain a higher efficiency in the removal of organic contaminants [9–11]. Although much effort has been devoted to the investigation of H₂O₂ photogen-

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eration [4–6,12–16], far less attention has been paid to the basic photochemical transformations of H_2O_2 in irradiated TiO_2 suspensions [11,14,17,18], and few of the papers give a detailed description of the observed kinetics [11,18]. Accordingly, the photolysis of H_2O_2 in the presence of semiconductors deserves more attention. Hence, we considered it useful to study the kinetic behavior of H_2O_2 in near UV-irradiated aqueous unbuffered TiO_2 suspensions, and to extend the examinations to the influence of essential reaction conditions such as the substrate concentration, the catalyst loading, the concentration of dissolved oxygen, and the irradiation intensity.

2. Experimental

Stabilizer-free H_2O_2 was purchased from Merck. TiO_2 (Aldrich, anatase > 99.9%, specific surface area $3.8 \text{ m}^2 \text{ g}^{-1}$ [19]) was used as received. Triple distilled water was utilized in all experiments. All chemicals were of analytical grade.

The suspensions were made by suspending TiO_2 in H_2O_2 solutions. The initial concentrations of H_2O_2 and TiO_2 were constant in all experiments, unless otherwise stated (ca. 0.01 M and 1 g l^{-1} , respectively). The reactions were carried out in a thermostated Pyrex cylindrical photoreactor (300 mm in length, 25 mm in diameter, 170 ml in volume), open to air (except in the case of evolved O_2 determinations), positioned in a black box. The suspension was maintained at $25 \pm 0.2^\circ\text{C}$ and stirred magnetically. Six 6-W medium-pressure mercury vapor lamps (with maximum emission at 365 nm) were mounted in movable positions around the reactor. (The UV cut-off of the Pyrex apparatus is at ca. 310 nm.) The photon flux was measured by potassium ferrioxalate actinometry [20]. The incident light intensity inside the reactor changed between 2.7×10^{-7} and 8.7×10^{-6} einstein $\text{dm}^{-3} \text{ s}^{-1}$. During the photodegradation of H_2O_2 , sampling was per-

formed at regular intervals. In the case of classical permanganometric analysis, the samples (5 ml) were acidified with 20% sulfuric acid (4 ml), and titrated with standard 0.02–0.002 M potassium permanganate solution. When the concentration of H_2O_2 was lower than 10^{-3} M, spectrophotometric determination was performed: after withdrawal, the samples were immediately centrifuged and/or filtered on Whatman Anotop 0.02 μm filters, and the absorbance of crystal violet formed through the oxidation of leuco crystal violet by H_2O_2 in the presence of horseradish peroxidase was measured at 592 nm [21]. The absorbance measurements were carried out on an HP 8452A diode array spectrophotometer. For the determination of evolved O_2 , gas chromatographic headspace analysis was performed (HP5890 series II GC equipped with a thermal conductivity detector and a Porapak QS column).

3. Results and discussion

The H_2O_2 concentration changes under different experimental conditions are shown in Fig. 1. In the presence of TiO_2 in a concentration of 1 g l^{-1} without UV irradiation, after mixing for 5 h in the dark, a decrease of ca. 1% in the

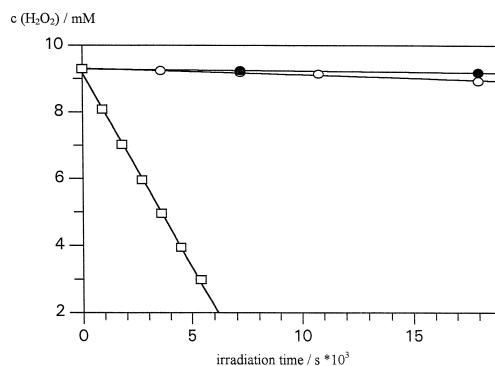


Fig. 1. Changes in H_2O_2 concentration under different reaction conditions in the presence of (O): $\text{UV} = 8.7 \times 10^{-6}$ einstein $\text{dm}^{-3} \text{ s}^{-1}$; (●): $\text{TiO}_2 = 1 \text{ g l}^{-1}$; (□): UV and TiO_2 (8.7×10^{-6} einstein $\text{dm}^{-3} \text{ s}^{-1}$ and 1 g l^{-1} , respectively).

H_2O_2 concentration was measured. In the UV-irradiated solution ($I = 8.7 \times 10^{-6}$ einstein $\text{dm}^{-3} \text{s}^{-1}$) without added TiO_2 , the (very slow) homogeneous photolysis could be satisfactorily described ($r_{\text{lc}} = 0.981$) by a formal zero-order rate constant of $(1.9 \pm 0.2) \times 10^{-8} \text{ M s}^{-1}$. In the presence of $1 \text{ g l}^{-1} \text{ TiO}_2$ and $I = 8.7 \times 10^{-6}$ einstein $\text{dm}^{-3} \text{s}^{-1}$ UV irradiation, a rapid decomposition of H_2O_2 was observed.

As these results reveal, the spontaneous (dark) decomposition and the photolysis of H_2O_2 are irrelevant, and efficient degradation was observed only in the presence of both TiO_2 and UV radiation. Both cited papers [11,18] report results that contrast with our findings relating to the homogeneous photolysis of H_2O_2 . Jenny and Pichat [18] found that heterogeneous H_2O_2 decomposition was only ca. $2.2 \times$ faster than homogeneous decomposition, while Augugliaro et al. [11] observed almost the same zero-order rate constant values for the decomposition in the absence and in the presence of TiO_2 ($9 \times 10^{-7} \text{ M s}^{-1}$ and $7.8 \times 10^{-7} \text{ M s}^{-1}$, respectively) in the presence of O_2 , while in the presence of He, the H_2O_2 decomposition was ca. three times faster in the heterogeneous system than in the homogeneous system. Since both groups used Pyrex apparatus or filters, the wavelength of the radiation reaching the reaction mixture was higher than 290 nm and, assuming that H_2O_2 has a rather low absorption cross-section in this region, the only reasonable explanation would be a rather high irradiation intensity. (It is noteworthy that many trace contaminants, e.g., metal ions, have an essential effect on H_2O_2 decomposition.)

As Fig. 2 shows, in the irradiated suspensions, the H_2O_2 concentration decreases linearly with reaction time, and the decomposition can be satisfactorily described by formal zero-order kinetics (for high conversions of H_2O_2 , a not too great, but significant deviation from linearity occurs). All the experimental runs carried out in this work gave a similar kinetic profile. The photochemical behavior of H_2O_2 under different reaction conditions was there-

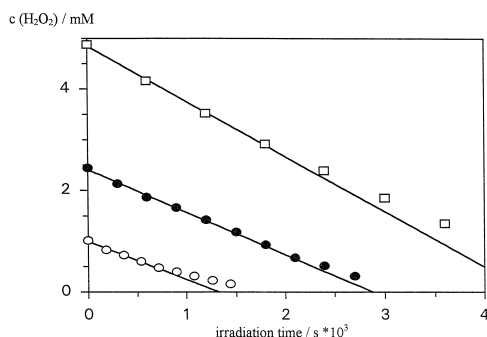


Fig. 2. H_2O_2 concentration vs. reaction time curves (○): $[\text{H}_2\text{O}_2]_0 = 1.02 \text{ mM}$; (●): $[\text{H}_2\text{O}_2]_0 = 2.44 \text{ mM}$; (□): $[\text{H}_2\text{O}_2]_0 = 4.88 \text{ mM}$. (The TiO_2 concentration and the irradiation intensity were constant at 1 g l^{-1} and 8.7×10^{-6} einstein $\text{dm}^{-3} \text{s}^{-1}$, respectively.)

fore subsequently described in terms of the initial rate of H_2O_2 decomposition (r_0), where the r_0 values were obtained from linear regression fits (by the least squares method with simple weighting) to the t_{irrad} vs. $c_{\text{H}_2\text{O}_2}$ curves. (The linear regression correlation coefficient (r_{lc}) values varied in the interval 0.993–0.999. The reproducibility of the initial rates calculated in this way was good; the standard deviation of the r_0 values for four experimental runs was less than 5%.)

The values of the initial decomposition rates at different initial H_2O_2 concentrations (measured at constant values of light intensity and TiO_2 concentration: 8.7×10^{-6} einstein $\text{dm}^{-3} \text{s}^{-1}$ and 1 g l^{-1} , respectively) are tabulated in Table 1. The initial rates decrease with decreasing initial H_2O_2 concentration.

The usual approach for the interpretation of this kind of surface reactions involves the Langmuir–Hinshelwood kinetics

$$r_0 = kK_L c_0 / (1 + K_L c_0) \quad (1)$$

where r_0 is the initial reaction rate, k is the reaction rate constant, and K_L and c_0 are the adsorption coefficient and the initial concentration of the reactant, respectively.

The linearization of Eq. (1) gives

$$1/r_0 = 1/(kK_L) \times 1/c_0 + 1/k \quad (2)$$

with an intercept of k^{-1} and a slope of $(K_L k)^{-1}$.

Table 1

Effect of the initial H_2O_2 concentration on the initial decomposition rate in the presence of TiO_2 in a concentration of 1 g l^{-1} and a light intensity of $8.7 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$

$c(\text{H}_2\text{O}_2)/\text{mM}$	$r_0/M \text{ s}^{-1} \times 10^{-7}$
1.02	7.5 ± 0.5
2.44	8.3 ± 0.4
4.88	10.9 ± 0.3
9.80	12.4 ± 0.4
43.56	17.8 ± 0.8
91.40	21 ± 1
898.40	29 ± 1

Our results (illustrated in Fig. 3) showed that the Langmuir–Hinshelwood kinetics did not fit the experimental data throughout the examined concentration range. Even at relatively high H_2O_2 concentration, when the assumption of $Kc_0 \ll 1$ is not reached, a deviation from linearity is observed. Because of the observed deviation to test our results, the Freundlich treatment was applied (which is more an empirical formula often used for the description of the adsorption in solutions) on the basis of Eq. (3):

$$r_0 = kK_F c_0^n \quad (3)$$

where r_0 , c_0 , k and K_F have similar meanings as in the case of Langmuir–Hinshelwood kinetics, while n characterizes the strength of adsorption. (Although the theoretical background is

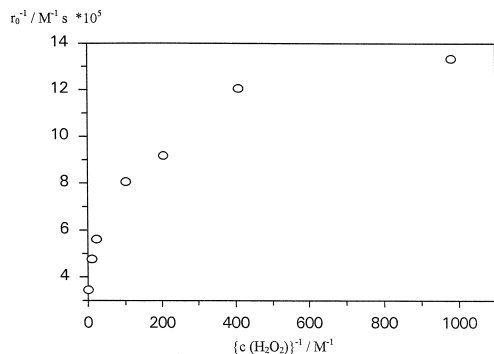


Fig. 3. Linearized Langmuir–Hinshelwood plot of the initial rate of H_2O_2 decomposition as a function of the initial H_2O_2 concentration. (The TiO_2 concentration and the irradiation intensity were constant at 1 g l^{-1} and $8.7 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$, respectively; for more details, see text.)

not so well-founded in the case of Freundlich isotherm, the experimental results often give better agreement with this model [22].)

A plot of $\log r_0$ vs. $\log c_0$ should give a straight line, as evidenced by the following equation:

$$\log r_0 = \log kK_F + n \log c_0 \quad (4)$$

The experimental data can be satisfactorily described ($r_{lc} = 0.991$) by the Freundlich model, as Fig. 4 demonstrates. The slope of the curve gave 0.21 ± 0.01 for the value of n . If it is taken into account that the apparent reaction rate (r) can be generally formulated as

$$r = -dc/dt = k \times c^n \quad (5)$$

integration results in

$$c^{1-n} = c_0^{1-n} - k \times t(1-n) \quad (6)$$

On the basis of Eq. (6), computer simulation was performed to justify the validity of the results. All the experimental data were in good accordance with the calculated concentrations (the mean relative deviation was 4.6%) and the rate obtained for maximum surface coverage $3.2 \times 10^{-6} \text{ M s}^{-1}$ was quite close to the experimental value of $(2.9 \pm 0.1) \times 10^{-6} \text{ M s}^{-1}$ measured at the highest applied concentration of H_2O_2 . With these considerations in mind, it can be concluded that the observed formal zero-order kinetics may be explained in that, even at a low concentration of H_2O_2 , a nearly fully covered

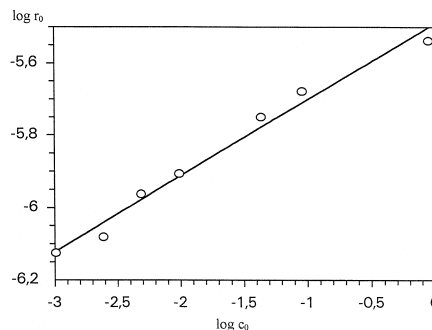
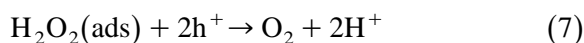


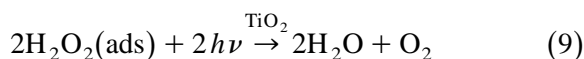
Fig. 4. Application of the Freundlich model Eq. (4) to the effect of the initial H_2O_2 concentration on the initial rate of H_2O_2 decomposition (slope: 0.21 ± 0.01).

surface can be reached, although increasing H_2O_2 content results in an enhanced surface coverage. This assumption is supported by the fact that a significant adsorption of H_2O_2 was not measured in the applied concentration range. Since the H_2O_2 molecules that decompose on the surface are replaced from the solution, the surface coverage can remain constant up to relatively high conversions.

The decomposition of H_2O_2 can be described [4–6,14,15] by



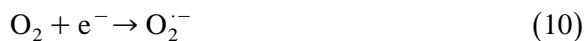
where the overall stoichiometry for H_2O_2 phototransformation in irradiated TiO_2 suspensions is



Since during the photodegradation of H_2O_2 , no change in pH was observed both the oxidation (Eq. (7)) and the reduction (Eq. (8)) processes must take place practically with the same rates on the surface of the catalyst. The observation that the presence of dissolved oxygen as an efficient electron scavenger caused no measurable change on the degradation rate of H_2O_2 —as discussed below—indicates that the H_2O_2 is the dominant charge acceptor species on the surface of the catalyst.

For determination of the O_2 formed, a series of gas chromatographic headspace analyses were performed, where the initial concentration of H_2O_2 was ca. 0.09 M, and the catalyst loading and irradiation intensity were 1 g l^{-1} and $8.7 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$, respectively (the reactor, similar to that used in the other experiments, was sealed by a silicone rubber septum and bubbled with Ar gas prior to irradiation). The only gas-phase product detected was O_2 (apart from water vapor), but only a fraction of the calculated (Eq. (9)) amount could be measured, due to the photoadsorption process [23–26].

Via reaction (10), the oxygen might compete with H_2O_2 in the process of electron capturing:



In this case, enhancing the amount of dissolved oxygen should cause a decrease in the H_2O_2 degradation rate, as was observed by Augugliaro et al. [11]. In our system, changing the concentration of dissolved oxygen (by continuously bubbling N_2 , air or O_2 through the suspensions) had no significant effect on the rate of phototransformation of H_2O_2 . Our measurements, illustrated in Fig. 5, revealed that the differences between the O_2 -free, the air-equilibrated and the O_2 -saturated systems were practically within the range of experimental error. This indicates that H_2O_2 can act either as an electron donor (Eq. (7)) or as an electron acceptor (Eq. (8)) and in the electron-capturing process, O_2 can not compete efficiently with H_2O_2 for the photogenerated electrons.

In the heterogeneous photocatalytic processes, the amount of photocatalyst added has a great influence on the photodegradation efficiency. For a study of the effect of the catalyst on the H_2O_2 phototransformation, the TiO_2 loading was varied in the concentration range $0\text{--}5 \text{ g l}^{-1}$ at constant values of light intensity and initial H_2O_2 concentration ($8.7 \times 10^{-6} \text{ einstein dm}^{-3} \text{ s}^{-1}$ and 0.01 M, respectively). The reaction rates increased linearly with increasing

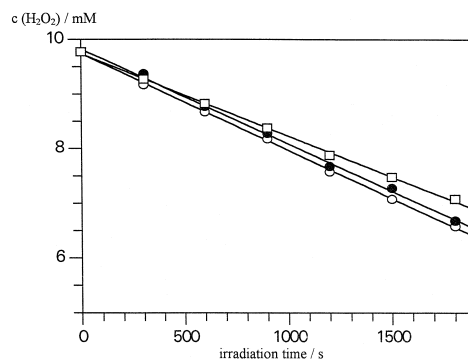


Fig. 5. Effect of the dissolved oxygen concentration on the H_2O_2 degradation rate in the presence of (○): N_2 $r_0 = (1.77 \pm 0.08) \times 10^{-6} \text{ M s}^{-1}$; (●): O_2 $r_0 = (1.73 \pm 0.07) \times 10^{-6} \text{ M s}^{-1}$; (□): air $r_0 = (1.50 \pm 0.1) \times 10^{-6} \text{ M s}^{-1}$.

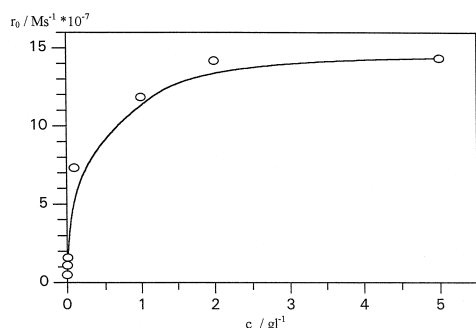


Fig. 6. Effect of the TiO_2 concentration on the initial H_2O_2 degradation rate at constant values of light intensity (8.7×10^{-6} einstein $\text{dm}^{-3} \text{s}^{-1}$) and initial H_2O_2 concentration (ca. 0.01 M).

TiO_2 loading up to 0.1 g l^{-1} , and then gradually leveled off. The 'saturation-type' behavior observed (Fig. 6) is quite usual in similar systems [27,28] and it is understandable if it is taken into account that increasing catalyst loading results in an increased number of active sites available for the decomposition of substrate molecules. This enhancement might be limited by the concentration of the substrate (as discussed before) and by the photons impinging on the suspension to activate the semiconductor. To test the latter possibility, the influence of the irradiation intensity on the degradation rate was examined at a catalyst loading of 1 g l^{-1} and a H_2O_2 concentration of ca. 0.01 M. (The intensity was changed by varying the number of UV lamps and their distance from the reactor.) As Fig. 7 shows, the experimental data satisfactorily fitted a straight line ($r_{lc} = 0.988$, slope =

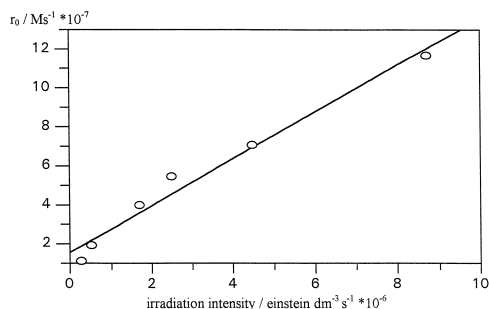


Fig. 7. Effect of the irradiation intensity on the initial H_2O_2 degradation rate at constant values of catalyst loading (1 g l^{-1}) and initial H_2O_2 concentration (ca. 0.01 M).

0.12 ± 0.01). Therefore, it may be concluded that the observed H_2O_2 photodecomposition is determined by the UV photons impinging on the suspension. Under the applied experimental conditions, only the lower intensity range could be tested where the initial rate scales linearly with the irradiation intensity, while at very high photon flux, the reaction rate usually varies with the square root of the intensity [22,29–31] (the wide plateau in the plot in Fig. 6 indicates that, after a certain amount of catalyst has been added, a further increase does not result in an enhanced scattering or shielding effect by the solid semiconductor particles in the apparatus used).

4. Conclusions

The rapid photocatalytic decomposition of H_2O_2 was observed in a UV-irradiated aqueous TiO_2 suspension. It was found that the heterogeneous decomposition can be satisfactorily described in terms of the initial rates obtained from linear regression fits to the t_{irrad} vs. $c_{\text{H}_2\text{O}_2}$ curves. The linear dependence observed between the irradiation intensity and the phototransformation rate demonstrates that the photons absorbed by the semiconductor particles determine the decomposition rate. The initial rate of decomposition of H_2O_2 is strongly affected by the catalyst loading up to a saturation limit. This is due to the increased number of active sites until all the photons reaching the reactor are absorbed by the semiconductor. For a description of the dependence of the initial rates on the initial concentrations, Langmuir–Hinshelwood and Freundlich treatments were applied. The Freundlich treatment proved to be a suitable model for the characterization of this reaction system, as evidenced by the good agreement between the calculated and the experimental data in the investigated concentration range. A decomposition rate was established with a formal reaction order of 0.21 ± 0.01 , as a

consequence of the adsorption of H_2O_2 on the surface of the photocatalyst. Dissolved oxygen as a potential electron scavenger does not have a significant effect on the degradation rate.

Consequently, the H_2O_2 presumably formed in irradiated TiO_2 suspensions may be expected to be only a short-lived intermediate, which can not accumulate under the applied conditions.

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