Photocatalytic Splitting of Liquid Water by n-TiO$_2$ Suspension

Waltraud Vonach and Nikola Getoff
Institut für Theoretische Chemie und Strahlenchemie der Universität Wien and Ludwig Boltzmann Institut für Strahlenchemie, Wien, Austria

Z. Naturforsch. 36a, 876—879 (1981); received July 9, 1981

By illumination ($\lambda > 300$ nm) of a suspension of n-TiO$_2$ (grain size $\leq 0.06$ mm, 3 to 15 mg/ml) in aqueous acid solutions, containing $10^{-3}$ mol $\cdot$ dm$^{-3}$ Ce$^{4+}$-ions an enhanced evolution of oxygen is observed. Its yield is dependent on the amount of TiO$_2$ in the suspension and on the temperature. Using n-TiO$_2$ suspended in diluted sulfuric acid, hydrogen and oxygen were produced in a ratio of about 2:1. In both systems n-TiO$_2$ is acting as an efficient electron donor. For the explanation of the processes probable reaction mechanisms are proposed.

1. Introduction

The catalytic photodissociation of water can be principally achieved by various redox couples, when their redox potential, $E^\circ > 1.23$ V [1]. In an earlier work Heidt and McMillan [2—4] demonstrated the evolution of hydrogen ($Q(H_2) < 10^{-3}$) from water by illumination of aqueous acid cerous solutions with u.v.-light (254 nm; reaction 1). As a result ceric ions were formed, which produce oxygen under irradiation with light of 300—400 nm (reaction 2):

$\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ce}^{4+} + \text{OH}^- + 1/2 \text{H}_2$ \hspace{1cm} (1)

$4 \text{Ce}^{4+} + 2 \text{H}_2\text{O} \rightarrow 4 \text{Ce}^{3+} + 4 \text{H}^+ + \text{O}_2$ \hspace{1cm} (2)

The ceric ions can also be reduced thermally ($> 30^\circ$C) [5]. Kiwi and Grätzel [6] succeeded to increase the oxygen yield by adding certain redox catalysts (PtO$_2$ or IrO$_2$). They observed for the formation of oxygen a rate of

$k = 3 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$ $\cdot$ h$^{-1}$

and for the ceric ion reduction,

$k = 1.2 \times 10^{-1}$ mol $\cdot$ dm$^{-3}$ $\cdot$ h$^{-1}$.

Further it was reported [7] that small amounts of H$_2$ and O$_2$ were produced by splitting of gaseous water over TiO$_2$ under illumination, but this effect was afterwards seriously doubted [8]. Recently, however, it was shown [9] that gas phase water can be photolysed ($\lambda > 320$ nm) to H$_2$ (11 µmole per 100 mg oxides and 20 h) and O$_2$ in the presence of a TiO$_2$/RuO$_2$ (8:2) mixture at room temperature. In addition it was observed [10, 11] that platinized TiO$_2$ powder acts as a photocatalyst, initiating the formation of CO$_2$ and H$_2$ from gaseous water and active carbon or converting C$_2$H$_4$ and gas phase water into C$_2$H$_4$, CO$_2$, CH$_4$ and H$_2$. Thereby it was assumed that Pt is working as a cathode and TiO$_2$ as photoanode, similar to the photoelectrochemical cells. Platinized powdered TiO$_2$ is able to split gaseous water ($\sim 21$ Torr) or in the presence of active carbon to promote the formation of H$_2$ and CO$_2$ [10, 11].

Recently we have reported the effect of n-TiO$_2$ powder, added as suspension to an aqueous acid ceric solution, on the oxygen evolution under light illumination [12]. The results of subsequent investigations on this subject are reported in this paper. It is shown that n-TiO$_2$ semiconductor is not only an efficient photoanode in a photoelectrochemical cell of the Fujishima-Honda-type [13, 14], but can also be applied as a photocatalyst in suspension, alone or in combination with other photo- and redox systems, e.g. Ce$^{4+}$/Ce$^{3+}$ for water dissociation under illumination.

2. Experimental

All chemicals (H$_2$SO$_4$, Ce(SO$_4$)$_2$, 4H$_2$O, p.a. Merck, Darmstadt) were used without further purification. Titanium dioxide powder (98% rutil) for technical purpose was first further milled (grain size $\leq 0.06$ mm) and then heated at 1150°C in a thyristor steered oven in air atmosphere for about 1 hour in order to convert it to rutil [14]. As radiation source a Hg-medium pressure lamp (HPK 125 W, Philips) was used in combination with a previously described $4\pi$-geometry double-wall vessel [15, 16]. It was equipped with a "Duran 500"...
filter, cutting off light with $\lambda < 300$ nm. The solutions (about 150 ml) were prepared using at least four times distilled water and were purged with high purity argon (Messer Griesheim, Vienna) for about 1 hour in order to remove oxygen. During irradiation the temperature was kept constant by means of a thermostat. The absorption spectra were measured with a spectrophotometer “Coleman 565” (Perkin Elmer). The evolved gas was collected by a vacuum line and analysed by gaschromatography.

3. Results and Discussion

For convenience both systems, Ce$^{4+}$/Ce$^{3+}$-$\text{TiO}_2$ and H$_2$SO$_4$/Ti$\text{O}_2$, will be treated separately.

3.1. The Ce$^{4+}$/Ce$^{3+}$-$\text{TiO}_2$ System

The previously observed effect on the photosensitized O$_2$-formation in an aqueous acid (0.5 mol $\cdot$ dm$^{-3}$ H$_2$SO$_4$) Ce$^{4+}$/Ce$^{3+}$ solution in the presence of n-Ti$\text{O}_2$ suspension [12], was now further investigated. The acid aqueous suspension consisting of Ce$^{4+}$-ions ($\lambda_{\text{max}} = 320$ nm, $\varepsilon_{320} = 4.7 \times 10^2$ m$^2$ $\cdot$ mol$^{-1}$) and Ti$\text{O}_2$ ($\lambda_{\text{max}} \approx 355$ nm) was illuminated under intensive stirring at 30 °C and the evolved gases were pumped out and analysed. Some experiments were performed also at 10 and 60 °C under otherwise equal conditions.

By irradiating of airfree solutions of $10^{-3}$ mol $\cdot$ dm$^{-3}$ Ce$^{4+}$ and 0.5 mol $\cdot$ dm$^{-3}$ H$_2$SO$_4$ for 15 min at 30 °C in the absence of n-Ti$\text{O}_2$ the observed oxygen yield did not exceed $0.2 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$ O$_2$. However, by adding n-Ti$\text{O}_2$ powder to the solution under the same experimental conditions the O$_2$ evolution rose rapidly, as can be seen in Figure 1. A maximum yield of about $8 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$ O$_2$ was obtained in the presence of 10 mg n-Ti$\text{O}_2$/ml solution of $10^{-3}$ mol $\cdot$ dm$^{-3}$ Ce$^{4+}$ and 0.5 mol $\cdot$ dm$^{-3}$ H$_2$SO$_4$. The decrease of the yield is probably due to the insufficient stirring under the experimental conditions and by the limited Ce$^{4+}$ concentration applied.

The O$_2$ formation was also studied as a function of irradiation time using 3 mg n-Ti$\text{O}_2$/ml solution, and the results are presented in Figure 2.

The obtained curve shows first a strong increase from $1.8 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$ O$_2$ at 5 min to above $6 \times 10^{-5}$ mol $\cdot$ dm$^{-3}$ O$_2$ about 50 min irradiation time and a steep decrease above 60 min. Following the concentration change of Ce$^{4+}$ in the solution at the same time spectrophotometrically it was found that the photoproduction of oxygen is proportional to the Ce$^{4+}$ consumption. This effect is demonstrated in Figure 3.

The observed formation of small amounts of oxygen in the absence of Ti$\text{O}_2$ powder in the Ce$^{4+}$ solution is based on the known reaction (2).

In order to explain the role of the n-Ti$\text{O}_2$ in the strongly enhanced photoproduction of oxygen from liquid water it is to be considered that part of the light ($\lambda > 360$ nm) is mostly absorbed by the semiconductor. As a result, each absorbed quantum promotes an electron from the valence band to the conductivity band (energy gap, $\Delta E \cong 3.1$ eV, $\lambda \leq 400$ nm):

$$\text{TiO}_2 \rightarrow \cdot \text{TiO}_2 \rightarrow (\text{TiO}_2^+ \cdot e^-).$$ (3)
Fig. 3. O₂-formation as a function of Ce⁴⁺-consumption (System: 10⁻³ mol · dm⁻³ Ce⁴⁺, 0.5 mol · dm⁻³ H₂SO₄; 3 mg n-TiO₂ powder/ml, at 30 °C). (a) O₂ at 10 °C, (b) at 30 °C and (c) at 60 °C, experimental conditions as above.

The transients (TiO₂⁺· e⁻) on the particle surface can act as electron donor, reducing the Ce⁴⁺ ions under formation of positively charged centres (so called p⁺ holes, TiO₂⁺), which can split the water, reforming n-TiO₂:

(TiO₂⁺· e⁻) + Ce⁴⁺ → TiO₂⁺ + Ce³⁺, (4)
4TiO₂⁺ + 2H₂O → 4TiO₂ + 4H⁺ + O₂. (5)

Thereby two individual reaction steps are assumed:
a) Reaction of water molecules with positively charged holes (p⁺) on the surface of each individual n-TiO₂ particle, where H₂O⁺ transients are formed. The last ones are known to be very reactive toward water molecules, leading to the formation of OH-radicals [17].

H₂O + TiO₂⁺ → TiO₂ + H₂O⁺, (6)
H₂O⁺ + H₂O → H₃O⁺ + OH. (7)

b) The OH-radicals are oxidized on the particle surface in a second reaction step, namely:

OH + TiO₂⁺ → TiO₂ + H⁺ + O, (8)
20 → O₂ (very fast). (9)

From the brutto equations (4) and (5) is obvious that the O₂ formation is dependent on the Ce⁴⁺ concentration (Figure 3). As mentioned above reaction (2) is temperature dependent. The role of this effect was studied by performing additional three series of experiments at 10, 30 and 60 °C (solution: 10⁻³ mol · dm⁻³ Ce⁴⁺, 0.5 mol · dm⁻³ H₂SO₄, 3 mg/ml n-TiO₂ powder, 45 min irradiation time). The mean O₂-yields are presented as (a) at 10 °C, (b) at 30 °C and (c) at 60 °C in Figure 3. It is obvious that with an increase of the temperature to 60 °C an enhanced O₂-yield is obtained (7 × 10⁻⁵ mol · dm⁻³ O₂), but about 90% Ce⁴⁺ is consumed. At 10 °C, however only about 50% Ce⁴⁺ is used up to produce 6 × 10⁻³ mol · dm⁻³ O₂, whereas the result at 30 °C lies on the line as expected. These facts indicate that at higher temperatures two processes are involved: photocatalytical and thermochemical. At low temperatures the catalytical process involving TiO₂ (reaction 4 to 9) is predominant.

The reaction mechanism is still not elucidated and further experiments are in progress.

3.2. The H₂SO₄/n-TiO₂ System

Considering the above discussed effect of n-TiO₂ suspension on the photochemical water oxidation a similar behaviour with other systems can be expected. As a further model for this purpose airfree solutions of aqueous sulfuric acid (10⁻³ to 1 mol · dm⁻³ H₂SO₄) in the presence of 5 mg/ml n-TiO₂ powder were irradiated. In this case the light (λ > 300 nm) was practically absorbed by TiO₂ only, since the diluted sulfuric acid absorbs below 300 nm, whereby ε₃₀(H₂SO₄) = 0.007. The experimental conditions were the same as described above. During the irradiation (45 min at 30 °C) the suspension was intensively stirred. The evolved gas mixture was collected by a vacuum line and analyzed by gaschromatography.

The aqueous H₂SO₄/TiO₂ system delivered under illumination hydrogen and oxygen, the yields of which increased with the concentration of sulfuric acid as shown in Figure 4.
It is of interest to note that the ratio of the $H_2/O_2$ yields is about 2. Based on this a consistent reaction mechanism is proposed. It is assumed that the $\text{TiO}_2^+ \cdot e^-$ species is acting as a very efficient electron donor for the $H_{aq}^+$, producing $H$-atoms, which combine to hydrogen molecules. Thereby the surface of the $\text{n-TiO}_2$ particles serves as an electron pool, where neutralization reactions take place.

\[
(\text{TiO}_2^+ \cdot e^-) + H_{aq}^+ \rightarrow H + \text{TiO}_2^+ ,
\]

\[
H + H \rightarrow H_2
\]

\[
(k_{12} = 1.15 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad [18]).
\]

\[
H + H_2O \rightarrow H_2 + OH
\]

\[
(k_{13} = 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \quad [19]).
\]

By reaction (10) a very active $\text{n-TiO}_2^+$ surface is formed, which initiates $O_2$ production according to reactions (5) to (9). Reaction (12) can play a role for the $H$-atoms diffused far away from the particle surface. Finally it is to be noted that two light quanta are needed for the splitting of 1 molecule $H_2O$ to hydrogen and oxygen.

It is to be mentioned that, using 0.5 mol $\cdot$ dm$^{-3}$ $\text{H}_2\text{SO}_4$ without addition of $\text{n-TiO}_2$ powder, very low yields for hydrogen ($\sim 0.3 \times 10^{-6}$ mol $\cdot$ dm$^{-3}$ $H_2$) and oxygen ($\sim 0.2 \times 10^{-6}$ mol $\cdot$ dm$^{-3}$ $O_2$) were obtained. This is due to the direct photolysis of the sulfuric acid, since [20]:

\[
\text{SO}_4^{2-} \rightarrow ^*\text{SO}_4^{2-} \rightarrow \text{SO}_4^- + e_{aq}^- ,
\]

Persulfuric acid is relatively by unstable and under illumination leads to $O_2$ formation and a mixture of sulfurous and sulfuric acids. This process (reactions 13 to 15) can be supressed by using light with $\lambda > 350$ nm.

4. Conclusions

Experimental evidence is presented for the ability of illuminated ($\lambda > 300$ nm) $\text{n-TiO}_2$ suspension to act as a very efficient electron donor, which is regenerable under proper experimental conditions. A photoinduced oxidation of water is observed, when $\text{Ce}^{4+}$ ions serve as electron acceptor in the presence of $\text{n-TiO}_2$. The $O_2$ yield is dependent upon temperature and the amount of added semiconductor. Using $H_{aq}^+$ as electron acceptor and $\text{n-TiO}_2$ as electron donor the water is split to $H_2$ and $O_2$ under the influence of light.

Acknowledgement

The authors like to express their appreciations to the Bundesministerium für Wissenschaft und Forschung and the Fonds zur Förderung der wissenschaftlichen Forschung in Austria for financial support, which rendered this work possible.