185. Visible Light-induced Oxygen Generation and Cyclic Water Cleavage Sensitized by Porphyrins

by **Enrico Borgarello, Kuppuswamy Kalyanasundaram, Yohmei Okuno**¹) and **Michael Grätzel**²)
Institut de chimie physique, Ecole Polytechnique Fédérale, Lausanne, Switzerland

(10.VII.81)

Summary

Zinctetramethylpyridylporphyrin ($ZnTMPyP^{4+}$) in acidic aqueous solution sensitizes efficiently oxygen generation by visible light in the presence of acceptors such as Fe^{3+}- and Ag^+-ions and colloidal RuO_2/TiO_2 redox catalyst. Hydrogen and oxygen are cogenerated under visible light illumination of $ZnTMPyP^{4+}$ solutions when a bifunctional catalyst (Pt and RuO_2 codeposited onto TiO_2) is employed.

Introduction. - The cleavage of water into hydrogen and oxygen through visible light irradiation of microheterogeneous systems is a fascinating research topic which is presently under intense investigation [1]. Apart from devices where low band gap colloidal semiconductors are employed as light harvesting units [2], the presence of sensitizers is required to achieve photolysis in the visible wavelength region. So far ruthenium complexes, $Ru(bipy)_3^{2+}$ and derivatives, have almost exclusively been employed for that purpose. Clearly, there is a need to enlarge the scope of viable redox chromophors.

Porphyrins appear to be an attractive choice for such water-cleavage sensitizer. The are cheap and easy to synthesize, absorb in the visible spectrum, dispose of long-lived excited states, and their redox potential can be tuned by suitable metal substitution to afford water decomposition. Photochemical reactions of porphyrins have already been widely investigated [3]. We [4] and others [5] have shown that water soluble porphyrins are extremely efficient sensitizers for light-induced hydrogen generation from water. However, these systems have so far been sacrificial in that instead of water an electron donor such as EDTA had been irreversibly consumed in the reaction.

This paper presents for the first time evidence for the redox-catalyzed oxygen generation from water sensitized by zinc porphyrin derivatives. Colloidal RuO_2 deposited onto TiO_2 is used to mediate water oxidation by the *Π*-cation of the porphyrin (P^+):

$$4\,P^+ + 2\,H_2O \xrightarrow{RuO_2} 4\,P + 4\,H^+ + O_2 \qquad (1)$$

---

¹) Visiting scientist from the Faculty of Pharmaceutical Sciences, Hokkaida University, Sapporo, Japan.

²) Author to whom correspondence should be addressed.

0018-019X/81/6/1937-06$01.00/0

Furthermore, the complete cycle of water cleavage sensitzed by porphyrin will be demonstrated.

Experimental. - Zinctetramethylpyridylporphyrin ($ZnTMPyP^{4+}$) and zinctetra(-*p*-sulfonato)phenylporphyrin ($ZnTPPS^{4-}$) were prepared according to a procedure described earlier [4] [6].

Two types of TiO_2 support materials were employed: the first, TiO_2-P25 *(Degussa)*, was kindly supplied to us by Dr. *P. Kleinschmidt, Degussa Zentralforschung*, Hanau, West Germany. This is a flame hydrolyzed material (anatase) characterized by a low surface hydroxyl population, a primary particle diameter of 140 Å and a surface area of 55 m^2/g. The second, TiO_2/RuO_2-U (*Sibit, Montedison*, Italy) is produced by acid digestion of titanium sulfate and is not calcined. The material (anatase) is characterized by a very high surface hydroxyl population, a particle size of approx. 500 Å and a surface area of 240 m^2/g. It is doped with 0.4% Nb_2O_5 and loaded with 0.1% RuO_2.

Loading of P-25 with RuO_2 was carried out by dispersing the TiO_2 in a RuO_4 solution. The TiO_2 concentration was usually 0.5 g/l and that of RuO_4 adjusted to the amount of loading required. The disperion was illuminated with light > 300 nm for approx. 30 min to bring about decomposition of RuO_4 according to:

$$RuO_4 \xrightarrow{h\nu} RuO_2 + O_2 \qquad (2)$$

The RuO_2 produced precipitates as an ultrafine layer onto the TiO_2 particles. A bifunctional redox catalyst consisting of Pt and RuO_2, codeposited on the TiO_2 particles, was used in cyclic water cleavage experiments. Loading with Pt was carried out after charging with RuO_2 according to a procedure described earlier [7].

Irradiations were performed with 15 ml solutions using a 450 W high-pressure Xe lamp as a light source. UV. and IR. radiation was removed by a 400 nm cut-off filter and a 15 cm water jacket, respectively. Hydrogen was analyzed by gas chromatography using a *Gow Mac* detector, carbosieve column (35°) and N_2 as a carrier gas. The formation of oxygen was measured either directly in the irradiated flask by means of an oxygen-specific electrode or by using the *Teledyne* fuel cell system described earlier [7]. A thermostated cell equipped with a water jacket containing 25 ml solution was employed for experiments at elevated temperature.

Results and Discussion. - Light-induced O_2 generation from water sensitized by water soluble porphyrins was first investigated using either Fe^{3+} or Ag^+ as electron acceptor. Aqueous solutions of $ZnTMPyP^{4+}$ (1.5×10^{-4} M) of pH 1.6 containing Fe^{3+} (2.5×10^{-2} M) and TiO_2-P25 catalyst produced efficiently oxygen under visible light irradiation *(Fig. 1)*. Rates of O_2 formation ($r(O_2)$) increase from 15 μl/h to 50 μl/h as

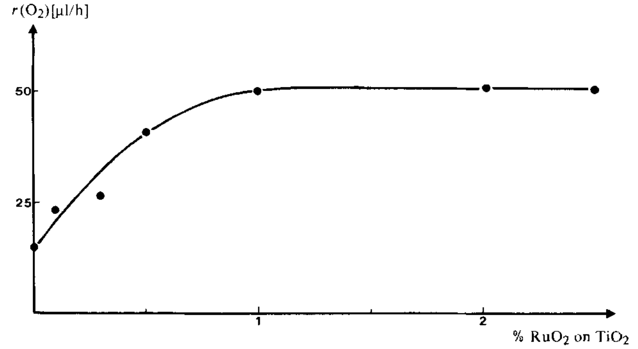

Fig. 1. *Effect of RuO_2 loading of the TiO_2 catalyst on the visible light induced oxygen generation from water sensitized by $ZnTMPyP^{4+}$* ($[ZnTMPyP^{4+}] = 1.5 \times 10^{-4}$ M, $[Fe^{3+}] = 2.5 \times 10^{-2}$ M, pH 1.6, $[TiO_2] = 500$ mg/l)

the RuO_2 loading of the catalyst increases from 0 to 1%. No oxygen is formed in the absence of TiO_2-P25 catalyst. Decreasing the $ZnTMPyP^{4+}$ concentration from 1.5×10^{-4} to 0.7×10^{-4} M results in a twofold decrease in the value of $r(O_2)$.

Increasing the pH to 2.5 lowers $r(O_2)$ by a factor of 5. A similar reduction is found when the pH is decreased to 0.8. Here rapid demetallization of the porphyrin[3]) renders the results ambiguous. At pH 1.6 the demetallization process does practically not occur during the first 5 hours. Over this period, a total of 7.4×10^{-4} mol/l O_2 was produced and an equivalent of 3×10^{-3} mol/l ferric ion reduced corresponding to a turnover number of 20 for the $ZnTMPyP^{4+}$.

If Ag^+ instead of Fe^{3+} is used as an electron acceptor, the optimum pH for light-induced O_2 generation is found to be around 4.5. At higher pH, precipitation of AgOH takes place. Visible light irradiation of a 15 ml solution (1.5×10^{-4} M $ZnTMPyP^{4+}$, 2.5×10^{-2} M Ag^+ and 500 mg/l TiO_2/RuO_2 (1%)) produces O_2 at a rate of 9 µl/h. A black deposit of Ag onto the TiO_2 particles becomes apparent during illumination. Comparison with the decrease in Ag^+ concentration determined analytically with the amount of O_2 produced showed a ratio of $> 3:1$, close to the expected stoichiometric 4:1 proportion.

Interestingly, when TiO_2-U (*Montedison*, anatase) is employed as a support material for RuO_2, efficient Fe^{3+}- and Ag^+-reduction sensitized by $ZnTMPyP^{4+}$ takes also place. However, only very small amounts of O_2 which are far below the stoichiometric ratio appear in the gas phase. In this case, the O_2 generated is almost totally bound to the TiO_2 which acts as an O_2 carrier. It can be released from the surface by addition of phosphate to the solution[4]).

Laser photolysis investigations carried out with solutions of $ZnTMPyP^{4+}$ and Fe^{3+} showed occurrence of oxidative quenching of the porphyrin triplet state

$$ZnTMPyP^{4+}\,(T_1) + Fe^{3+} \rightarrow Fe^{2+} + ZnTMPyP^{5+} \qquad (3)$$

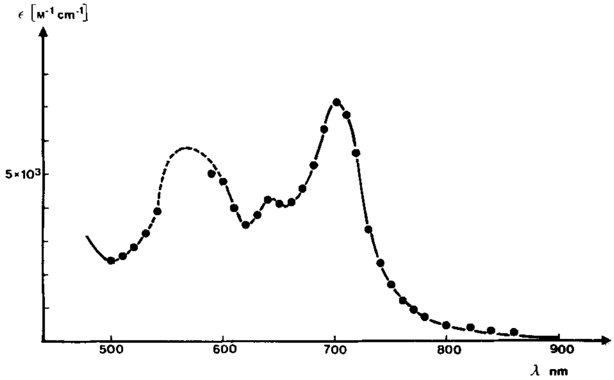

Fig. 2. *Transient spectrum obtained from the 530 nm laser photolysis of $ZnTMPyP^{4+}$ (1×10^{-5} M) in the presence of Fe^{3+} (2×10^{-3} M)* (Points taken 50 µs after the laser pulse)

---

[3]) The demetallated porphyrin sensitizes also O_2 generation from water albeit with smaller efficiency.

[4]) This will be treated in detail in a forthcoming paper.

The rate constant k_1 measured by varying Fe^{3+}-concentration is $1.3 \times 10^{10}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and the cage escape yield practically 100% at pH 2 (ionic strength $\sim 10^{-2}\,\mathrm{M}$). *Figure 2* shows the transient spectrum corrected for ground state porphyrin absorption obtained from the 530 nm laser photolysis of $ZnTMPyP^{4+}$-solutions in the presence of Fe^{3+}. Measurements were taken 50 µs after the laser pulse, *i.e.* after completion of reaction *(equ. 3)*. The spectrum is identical with that of the porphyrin Π-cation radical, $ZnTMPyP^{5+}$, for which absolute extinction coefficients were evaluated. The $ZnTMPyP^{5+}$ absorption disappears in the millisecond time domain due to back electron transfer to Fe^{2+}. The second-order rate constant for this process was evaluated as $5 \times 10^{7}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at pH 2.

On the basis of these observations, we postulate two parallel pathways operative in the light-driven and porphyrin-sensitized O_2 formation from Fe^{3+} (Ag^+) and water[5]).

$$4\,Fe^{3+}\,(Ag^{+}) + 2\,H_2O \xrightarrow{h\nu} 4\,Fe^{2+}\,(Ag) + O_2 + 4\,H^{+}$$

$$\Delta G^\circ = 33.7\ \mathrm{kcal/mol}\ (Fe^{3+/2+}/\mathrm{pH}\ 1.6) \qquad (4)$$

The first involves solution quenching of the porphyrin triplet state by Fe^{3+} followed by RuO_2 catalyzed O_2 generation from $ZnTMPyP^{5+}$ and water *(equ. 1)*. Evidently, our RuO_2/TiO_2 catalyst is active enough to intercept the back reaction between Fe^{2+} and $ZnTMPyP^{5+}$ which occurs in the millisecond time domain. Also, the RuO_2/TiO_2 micro particles appear to intervene specifically, thus avoiding short circuitry of this undesirable back electron transfer.

As a significant fraction of $ZnTMPyP^{4+}$ adheres to the surface of TiO_2, one has to envisage a second mechanism of O_2 formation, outlined in *Figure 3*. Here, the excited porphyrin injects a charge in the TiO_2 conduction band. Subsequently, the conduction band electron reduces Fe^{3+} to Fe^{2+} (or Ag^+ to Ag) while the RuO_2 deposit on the TiO_2 particle catalyzes O_2 formation from the oxidized porphyrin and water[6]). The fact that TiO_2 conduction band electrons are capable of interacting efficiently with Fe^{3+} and Ag^+ was independently verified by exciting TiO_2-P25 in

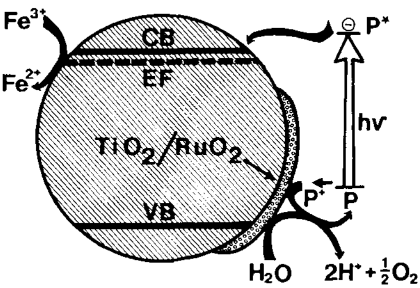

Fig. 3. *Schematic illustration of processes occurring during light induced oxygen generation from Fe^{3+} and water sensitized by $ZnTMPyP^{4+}$*

---

[5]) This reaction stores *ca.* 0.4 eV of the photon energy for each electron transferred (Fe^{3+}, pH 1.6).

[6]) The details of RuO_2/TiO_2 catalysis have been investigated recently [8].

the absence of porphyrins with band gap irradiation. The evolution of O_2 and reduction of the acceptor ions is readily apparent under these conditions and will be analyzed in detail in a forthcoming paper.

If the excited state of $ZnTMPyP^{4+}$ is capable of electron injection into the TiO_2 conduction band and the porphyrin Π-cation radical can produce O_2 from water, then the operation of a complete water cleavage system should be feasible. We performed this crucial test with a solution of $ZnTMPyP^{4+}$ (1.5×10^{-4} M) and TiO_2-P25 (500 mg/l) charged with 1% RuO_2 and 8% Pt (produced *via* citrate reduction of H_2PtCl_6 [9]). The latter catalyst is necessary to promote water reduction by TiO_2 conduction band electrons. Irradiation of 15 ml solution with visible light produces H_2 and O_2 at a rate of 15 and 6 µl/h, respectively. This can be sustained over a period of at least 6 hours. No H_2 or O_2 was produced in the absence of porphyrin. Also, the presence of both RuO_2 and Pt was required to achieve water photolysis by visible light [10].

Additional experiments were carried out with the porphyrin $ZnTPPS^{4-}$. The former sensitizer does not afford O_2 generation in the presence of either Fe^{3+} or Ag^+ ions and the TiO_2-P25 catalyst loaded with RuO_2. Also, it is inactive in sensitizing water decomposition in the presence of TiO_2-P25/Pt/RuO_2 bifunctional redox catalyst. This behaviour is attributed to the unfavorable redox potential of $ZnTPPS^{4-}$, +870 mV (*vs.* NHE) as compared to +1180 mV for $ZnTMPyP^{4+}$ [11]. Thus, in acidic solution water oxidation by the porphyrin Π-cation is possible only in the case of $ZnTMPyP^{4+}$.

In conclusion, the present study establishes the suitability of porphyrins to sensitize O_2 generation from water and to afford visible light induced water cleavage. This opens up a large choice of synthetic possibilities to enhance the adsorption of the porphyrin to the semiconductor particle and to finetune its redox potential in order to improve the performance of these systems.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung* and the *Ciba-Geigy* AG, Basel, Switzerland. We are grateful to Dr. *M. Visca* (*Sibit*, Montedison, Italy) and Prof. *E. Pelizzetti* (University of Torino, Italy) for supplying us with TiO_2-U. Also, we thank Dr. *P. Kleinschmidt* (*Degussa*, West Germany) for providing us a sample of TiO_2-P25. *Y. Okuno* thanks the *Naito Research Grant* 1980 for a traveling grant.

REFERENCES

[1] *A. Fujishima, A. & K. Honda*, Nature, *238*, 37 (1972); M. Calvin, Photochem. Photobiol. *23*, 425 (1976); *M. Calvin*, Acc. Chem. Res. *11*, 369 (1978); *V. Balzani, L. Moggi, M.F. Manfrin, F. Boletta & M. Gleria*, Science, *189*, 852 (1975); *K.I. Zamaraev & V.N. Parmon*, Catal. Rev. Sci. Eng. *22*, 261 (1980); *G. Porter & M.D. Archer*, Interdisc. Sci. Rev. *1*, 119 (1976); *J. Bolton*, Science, *202*, 705 (1978); *M. Grätzel*, Ber. Bunsenges, Phys. Chem. *84*, 981 (1980); *J. Kiwi, K. Kalyanasundaram & M. Grätzel*, 'Structure and Bonding', 1981; *K. Kalyanasundaram & M. Grätzel*, Nato Summer School on Photoelectrochemistry, Gent, 1980 (Belgium), Nato Advanced Studies Treatise.

[2] *K. Kalyanasundaram, E. Borgarello & M. Grätzel*, Helv. Chim. Acta, *64*, 362 (1981).

[3] *G.R. Seely & M. Calvin*, J. Chem. Phys. *23*, 1068 (1955); *G.R. Seely & K. Talmadge*, Photochem. Photobiol. *3*, 195 (1964); *D. Mauzerall*, 'The Porphyrins', D. Dolphin, ed., Vol. V, Part c, p. 53, Academic Press, 1978; *A. Harriman & G. Porter*, J. Chem. Soc. Faraday Transac. II, *75*, 1543 (1979); *F.R. Hopf & D.G. Whitten*, 'Porphyrins and Metalloporphyrins', Smith, K.M. (Ed.); Elsevier, Amsterdam, pp. 667-700 (1975).

[4] *K. Kalyanasundaram & M. Grätzel,* Helv. Chim. Acta, *63,* 478 (1980).
[5] *G. McLendon & D. Miller,* J. Chem. Soc. Chem. Commun *1980,* 533; *A. Harriman, G. Porter & M.C. Richoux,* J. Chem. Soc. Faraday Transac. *2,* 77, 833 (1981).
[6] 'Porphyrins', D. Dolphin, (Ed.), Academic Press (1979).
[7] *D. Duonghong, E. Borgarello & M. Grätzel,* J. Am. Chem. Soc. *103,* 4685 (1981).
[8] *c.f. R. Humphry-Baker, J. Lilie & M. Grätzel,* J. Am. Chem. Soc., in print.
[9] *J. Turkevich, K. Aika, L.L. Ban, I. Okura & S. Namba,* J. Res. Inst. Cat. Hokkaido University, *23,* 54 (1976); *J. Turkevich,* 'Electrocatalysis of Fuel Cell Reaction', Brookhaven Symp. Proceedings, p. 123 (1967).
[10] *E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca & M. Grätzel,* J. Am. Chem. Soc., in print; *J. Kiwi, E. Borgarello, E. Pelizzetti, M. Visca & M. Grätzel,* Angew. Chem. Int. Ed. Engl. *19,* 646 (1980).
[11] *M. Neumann-Spallart & K. Kalyanasundaram,* Z. Naturforsch. *36B,* 596 (1981).