

Photochemical oxidation of water with thin AgCl layers

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Abstract

Thin silver chloride layers on SnO₂-coated glass plates evolve oxygen in the presence of a small excess of Ag⁺ ions in aqueous solution, with a maximum evolution rate at pH 4–5. The system shows self-sensitization of photochemical O₂ evolution, which means that new photoactive colour centres are formed on near-UV illumination (340–390 nm) composed of reduced silver species. A non-linear dependence of the O₂ evolution rate on the light intensity at low intensities changes into a linear dependence in the medium range (above about 300 μW cm⁻²). The quantum yield per redox equivalent for O₂ evolution in the linear range is approximately 0.8 on illumination with UV light and the same on illumination with blue light (420–480 nm). It is approximately 0.5 in the green range (500–540 nm). A mechanism for O₂ evolution is discussed.

Keywords: Photochemical oxidation; Water; Thin AgCl layers; Self-sensitization; Oxygen evolution

1. Introduction

The photochemical oxidation of water to oxygen remains one of the most serious problems in the solar splitting of water into H₂ and O₂, which has been reviewed recently by Bard and Fox [1]. Vogel [2] was probably the first to demonstrate the photochemical oxidation of Cl⁻ to Cl₂ and to observe that aqueous silver chloride suspensions become acidic on irradiation with sunlight under certain conditions, but he did not mention photochemical O₂ evolution in this work. His and most of the later studies on the light sensitivity of silver halides were motivated by the fascinating invention of photography. Baur and Rebmann [3], however, studied the photochemical properties of silver chloride with the aim of photolysing water and reported minor O₂ evolution from water on UV irradiation. Metzner and coworkers [4,5] reinvestigated this system in an attempt to contribute to the understanding of the ability of natural photosystem II to evolve O₂. They observed significant photochemical O₂ evolution from silver chloride suspensions containing an excess of Ag⁺, showing a maximum sensitivity at about pH 5. The first silver photographs on paper were not fixed by thiosulphate, but were simply “stabilized” by excess halide ion, a procedure invented by Talbot around 1834. His papers were sensitized by first soaking in sodium chloride solution, and then brushing with an excess of silver nitrate solution. The key to success

was the observation that the paper was more sensitive to light where there was a deficiency of NaCl [6]. This parallels our finding that the photochemical O₂ evolution of Ag⁺-A zeolite suspensions at approximately neutral pH occurs on addition of Cl⁻ due to AgCl formation; at a certain level of AgCl formation, the O₂ evolution drops abruptly [7]. The photo-oxidation of water with AgCl colloids in the presence of an excess of Ag⁺ ions on UV irradiation was studied by Chandrasekaran and Thomas [8]. This route was abandoned because of the low quantum yield observed in their experiments and because of the necessity to reoxidize the reduced silver, should the process become applicable in a solar energy conversion device. We became interested in the water oxidizing ability of Ag⁺-A zeolite-containing systems when we observed that self-sensitization takes place: as the reaction proceeds, the sensitivity is extended from near-UV-visible wavelengths towards the red range [9,10]. However, the critical parameters controlling this interesting reaction remained obscure. Therefore we prepared pure zeolite A [11], and investigated the photochemical and photophysical properties of Ag⁺-A zeolite monograin layers based on pure zeolite A samples [12]. From the results obtained, we concluded that the commercial zeolite A used in earlier experiments contained some Cl⁻, which plays a crucial role in the water photo-oxidation reaction [7]. Furthermore, we assumed that O₂ evolution occurs on silver chloride at the surface of the particles [12]. This finding made it necessary to reinvestigate the photochemical properties of AgCl with

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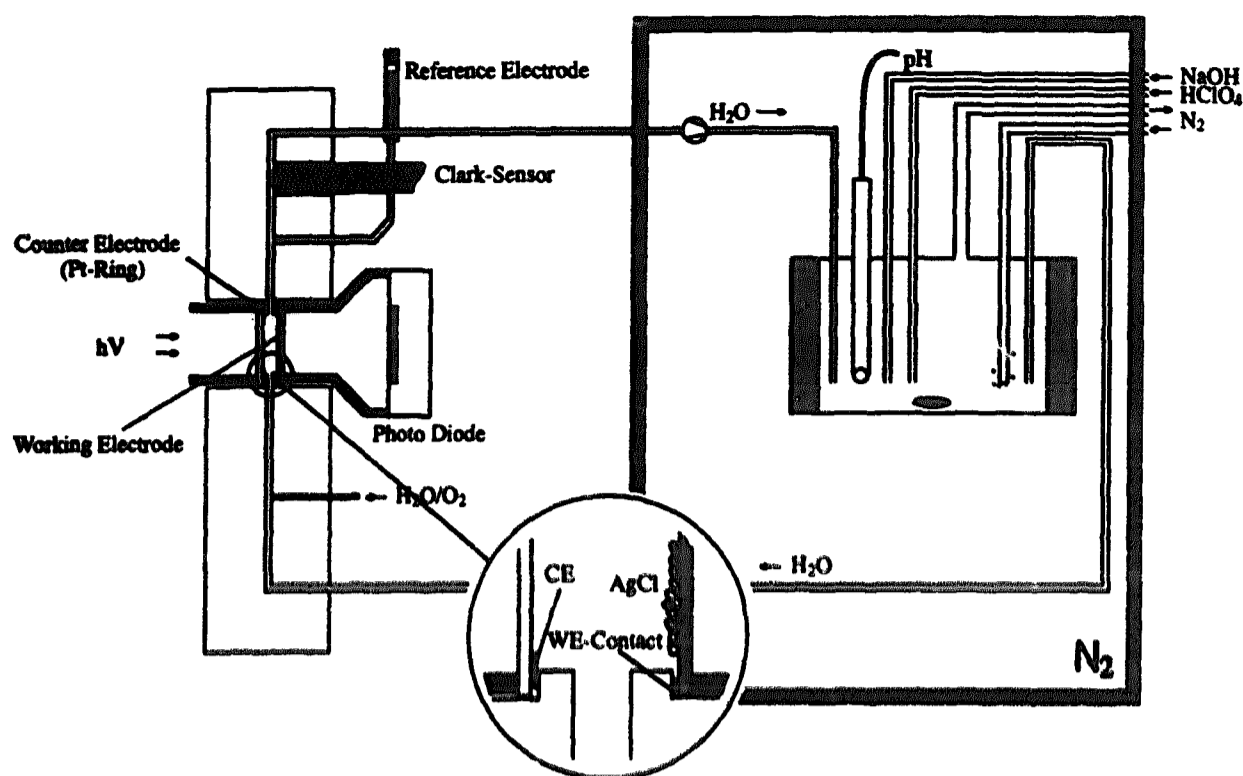


Fig. 1. Apparatus for photochemical experiments on thin layers. Left: photocell with a Clark O_2 sensor, a photodiode behind the reaction window, a capillary for H_2O/O_2 injection for calibration of the Clark sensor and an integrated three-electrode system for electrochemical experiments. Right: water reservoir with N_2 bubbler, pH electrode and acid/base injection in an N_2 -purged box. A pump transports the solution from the reservoir via a capillary system through the cell back to the reservoir.

respect to the water oxidation reaction. In this report, we focus on four parameters which have been found to be important: pH, Ag^+ to Cl^- ratio, wavelength and light intensity. We also give the quantum yield of photochemical O_2 evolution.

We have already stated that the driving force for the interest in the photosensitivity of silver halides was the photographic process. Therefore the behaviour of the photoelectrons, responsible for latent image formation and silver printouts, was studied very carefully [13–16]. The photoholes are assumed to be responsible for the losses due to recombination of the light-generated charge carriers and to reoxidation of latent image specks on the surface of silver chloride. Their mobility [17] and self-trapping [18] have therefore been investigated [16]. These and other studies motivated by photography may become important for the water splitting process. An interesting discussion on this subject was given by Levy [19].

2. Experimental details

2.1. Sample preparation

Zeolite A containing silver chloride complexes $((Ag^+)_n(Cl^-)_x-A$ zeolite, where n and x refer to one unit cell) was prepared as described in Ref. [7]. Thin layers of silver chloride on SnO_2 -coated glass plates were prepared by precipitation from equimolar amounts of silver nitrate and sodium chloride in the dark. After settling of the silver chloride, an excess of silver nitrate or sodium chloride ($5 \times 10^{-3} \text{ mol l}^{-1}$) was added to the solution above the layer in order to prepare $AgCl/Ag^+$ and $AgCl/Cl^-$ respectively. The layers contained approximately 100 mg silver chloride on an

area of about 1 cm^2 . They were dried at 70°C and fixed with $50 \mu\text{l}$ of a polystyrene-THF solution containing 6 mg ml^{-1} polymer. Silver oxide was precipitated from $0.1 \text{ M } AgNO_3$ by addition of $0.1 \text{ M } NaOH$ and was dried and fixed as described above. All chemicals used were of analytical grade. Doubly distilled water was used.

2.2. Photochemical experiments

The photochemical experiments with the $(Ag^+)_n(Cl^-)_x-A$ zeolite were carried out as described in Ref. [7] with a suspension of 200 mg zeolite in 250 ml of an N_2 -purged $0.1 \text{ M } NaNO_3$ solution at pH 6. The Cl^- concentration was monitored by adding various amounts of $1 \text{ M } NaCl$. Photochemical O_2 evolution and the concentration of free Cl^- in the solution were measured in situ with a Clark O_2 sensor (WTW EO 96 with a modified water tight head) and a Cl^- sensitive electrode (Orion, model 94-17B) respectively in a set-up similar to that described in Ref. [9]. In these experiments, IR-filtered and intensity-regulated white light from a 1000 W xenon high pressure lamp (PTI) was used (total radiant power, approximately 20 mW). The irradiated surface was approximately 35 cm^2 . Only part of the light was absorbed by the suspension.

The experiments with thin silver chloride layers on SnO_2 -coated glass plates were performed in an apparatus based on the principle described in Ref. [10] and illustrated in Fig. 1. The whole apparatus was kept in a box flushed with N_2 to minimize the background oxygen level. O_2 was detected in situ with a Clark O_2 sensor which was calibrated by injecting small precise amounts of air-saturated water. The signals depended linearly on the amount of injected O_2 down to very small concentrations, and the sensitivity was better than 1 ng

O_2 due to the small reaction volume of approximately 0.8 ml. The photoreactor was made of PCTFE, which is chemically and electrically inert. It was equipped with a three-electrode system for electrochemical measurements. A solution containing 0.1 M $NaNO_3$ and 10^{-3} M of the excess ion, Ag^+ or Cl^- for experiments with the $AgCl/Ag^+$ or $AgCl/Cl^-$ system respectively, was pumped via glass capillaries through the photoreactor from a reservoir of 130 ml, which was deoxygenated by N_2 (99.995%) bubbling. The pH in the thermostatically controlled reservoir was measured with a double junction pH electrode with saturated KNO_3 as outer electrolyte to stop Cl^- from diffusing into the reaction volume. The solutions had a pH of 5–6 which was not adjusted unless stated otherwise. In the experiments in which it was adjusted, this was done by injecting appropriate amounts of 0.1 M $NaOH$ or 0.1 M $HClO_4$. A 450 W Xe high pressure lamp was used as light source. The intensity-regulated light was IR-filtered and the wavelength band was selected by a set of broad-band interference filters: 340–390 nm (Balzers K36) for UV light; 430–480 nm (Balzers K45) for blue light; 500–540 nm (Balzers K3) for green light. The light passed through a quartz beam splitter, generating reference and main light beams which were directed to the photoreactor. Two Si photodiodes, one for reference and the other behind the sample, were tested to correlate linearly over the whole intensity range applied in our experiments. The photodiode behind the sample was used to calibrate that in the reference beam in the absence of a sample. In the presence of a sample no light reached the photodiode behind it due to absorption and reflection.

3. Results and discussion

The influence of the addition of $NaCl$ to a suspension of $(Ag^+)_n(Cl^-)_x-A$ zeolite has been reported recently [7]. The addition of $NaCl$ enhances the photochemical oxidation of water to O_2 up to a critical concentration above which the signal drops rapidly to zero. The luminescence of $(Ag^+)_6(Cl^-)_2-A$ zeolite at 600–700 nm, with a lifetime of the order of 100 μs at $-170^\circ C$, has been observed [12]. We report the results of a similar experiment in which the concentration of Cl^- was monitored in situ. Fig. 2 shows the amount of added $NaCl$ in millimoles, the free Cl^- measured in the suspension and the integrated amount of O_2 evolved over an irradiation period of 5 min. We observe that the O_2 signal first increases steeply on addition of $NaCl$, reaches a maximum and then falls off to zero as soon as a significant amount of free Cl^- appears in the suspension. At the beginning, silver chloride is formed, so that no free Cl^- is measured in the solution. The Ag^+ in the zeolite is mobile, while the Cl^- is occluded at room temperature. Ag^+ is ion exchanged on addition of $NaCl$ and goes to the surface. This means that the zeolite serves as a reservoir for Ag^+ . We have already stated that O_2 evolution is assumed to occur at the silver chloride present at the surface of the particles, which is essen-

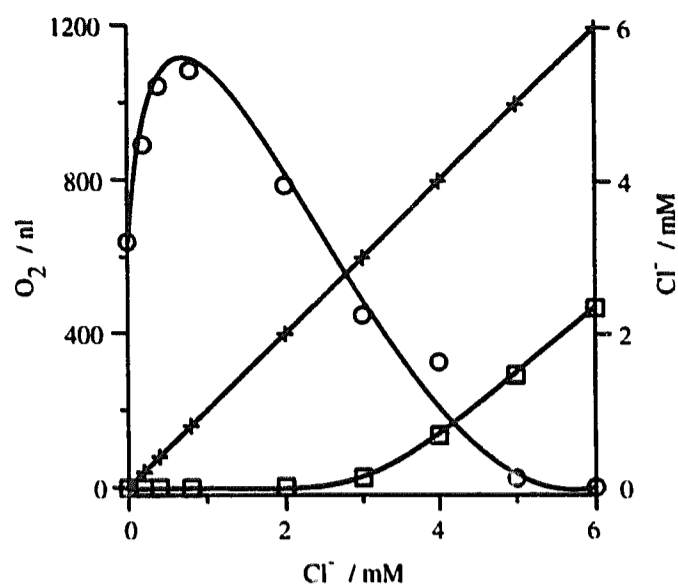


Fig. 2. Photochemical O_2 evolution of an $(Ag^+)_n(Cl^-)_x-A$ zeolite suspension at approximately pH 6 as a function of the added amount of $NaCl$: +, added amount of $NaCl$; \square , free Cl^- measured in the suspension; \circ , integrated O_2 signals over 5 min irradiation periods.

tial for the photochemical behaviour of the system [12]. This has been supported by X-ray diffraction experiments which indicate the presence of silver chloride on the surface of the $(Ag^+)_n(Cl^-)_x-A$ zeolite samples. As soon as free Cl^- is present, the system changes from $AgCl/Ag^+$ to $AgCl/Cl^-$ which has very different properties.

A study of the pH dependence of the photochemical properties of $AgCl$ and $AgCl$ on Ag^+-A zeolite, both in the presence of a large excess of Cl^- , shows that, under acidic conditions, Cl_2 is evolved with a high quantum yield and O_2 signals appear only in the strongly alkaline region [20,21]. Based on these observations, we built an $\{Ag^+/AgCl||Cl^-/Cl_2\}$ photogalvanic cell with an experimental open circuit potential of 1.05 V, but poor power/voltage behaviour [21,22]. We have reinvestigated the pH dependence of photochemical oxygen evolution at thin silver chloride layers on SnO_2 -coated glass plates. The main results of these experiments are reported in Fig. 3, where the O_2 evolution integrated over an irradiation period of 5 min is shown on UV illumination (350–390 nm) in 0.1 M $NaNO_3$ electrolyte in the presence of 10^{-3} M Ag^+ ion excess and in the presence of 10^{-3} M Cl^- excess; the two cases are named $AgCl/Ag^+$ and $AgCl/Cl^-$, respectively. The $AgCl/Ag^+$ system shows a maximum photochemical oxidation of water to O_2 at pH 4–5. No O_2 evolution was observed under alkaline conditions. This finding parallels the pH dependence of light-induced O_2 production by an aqueous $AgCl/AgNO_3$ system reported by Metzner and Fischer [4]. However, the $AgCl/Cl^-$ system shows no O_2 evolution under acidic and neutral conditions, and significant O_2 signals were only observed at above pH ≈ 10 , as expected from our earlier studies [20]. We may ask if the O_2 evolution under these basic conditions is due to the formation of silver oxide Ag_2O . In the presence of an excess of Cl^- , however, Ag_2O is thermodynamically unstable with respect to $AgCl$ even at pH 12 [23]. Nevertheless, we carried out photochemical experiments with silver oxide at pH 11 under the same conditions, but no O_2 formation was

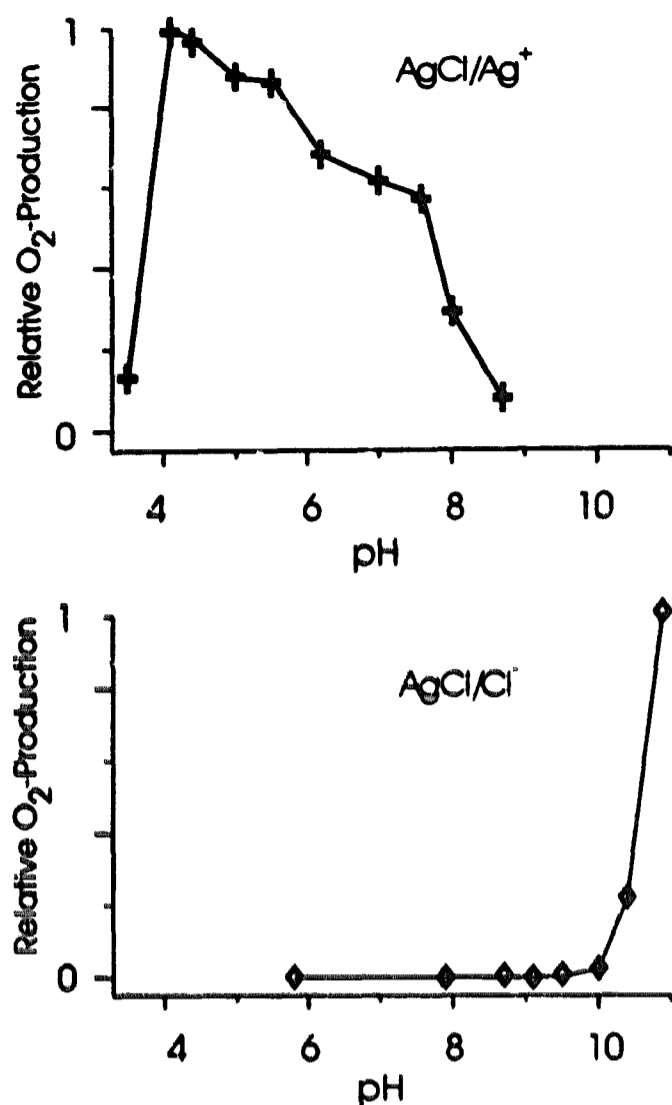


Fig. 3. pH dependence of O₂ evolution at thin silver chloride layers on SnO₂-coated glass plates on UV illumination. Top: AgCl/Ag⁺. Bottom: AgCl/Cl⁻.

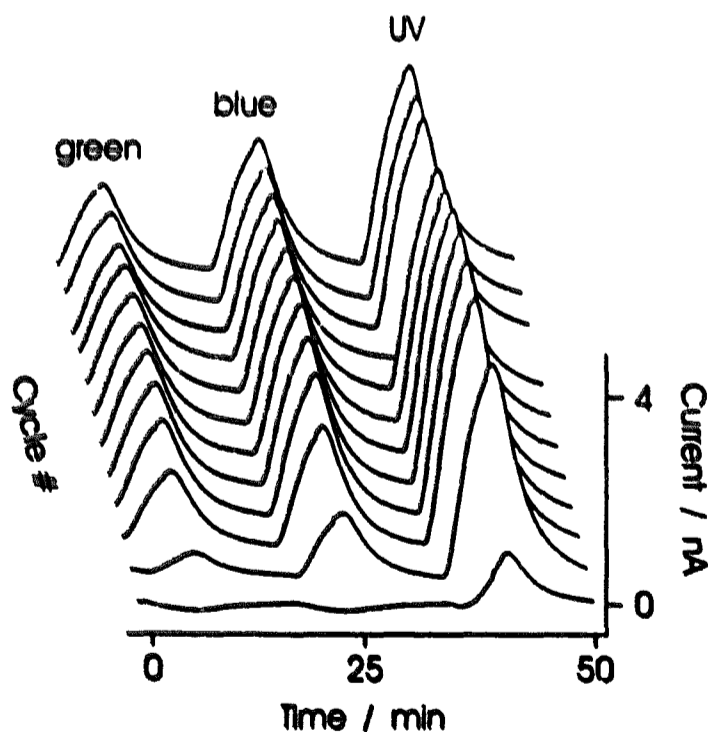


Fig. 4. Self-sensitization of the photochemical oxidation of water to O₂ on AgCl/Ag⁺ layers on SnO₂-coated glass plates. The signals of the O₂ detector are shown as a function of time, and the number of cycles start with the first cycle at the bottom. The samples were irradiated consecutively with green (500–540 nm), blue (430–480 nm) and UV (340–390 nm) light.

observed. Therefore it is safe to exclude Ag₂O as being responsible for the photochemically induced O₂ evolution of the AgCl/Cl⁻ system under alkaline conditions.

The self-sensitization process of the water oxidizing ability of some Ag⁺-containing systems is especially interesting. We have therefore checked whether the thin silver chloride layers on SnO₂-coated glass plates show this behaviour. This process is illustrated in Fig. 4 where we show the O₂ signals plotted vs. time for each irradiation cycle, starting with the first cycle at the bottom. In these experiments, each cycle started with a 5 min illumination period with green light, followed by illumination with blue light and then UV light. The intensity was 490 μW cm⁻² for green light, 400 μW cm⁻² for blue light and 70 μW cm⁻² for UV light. Each illumination period was followed by a dark period of 12 min during which the O₂ signals were allowed to decay to the background level. No O₂ evolution was detected on illumination with visible light and the signal on UV illumination was small in the first cycle. In the second and subsequent cycles, AgCl/Ag⁺ becomes increasingly light sensitive in the visible part of the spectrum. This means that AgCl/Ag⁺ layers on SnO₂-coated glass plates show the same type of self-sensitization behaviour as reported previously [9,10,24].

The photochemical oxidation of water to O₂ is a four-electron process and the question arises as to how it depends on the light intensity. The sensitivity of our experiment allowed us to investigate this problem down to low O₂ evolution rates. A typical result obtained for AgCl/Ag⁺ layers on SnO₂-coated glass plates is reported in Fig. 5, where we show the stationary O₂ evolution rates observed on illumination with blue light (430–480 nm) as a function of the light intensity. The sample was first illuminated with 100 μW cm⁻² UV light for 5 min in order to sensitize it for visible light. We observe a non-linear dependence of the O₂ evolution rate on the intensity at low light intensities, which

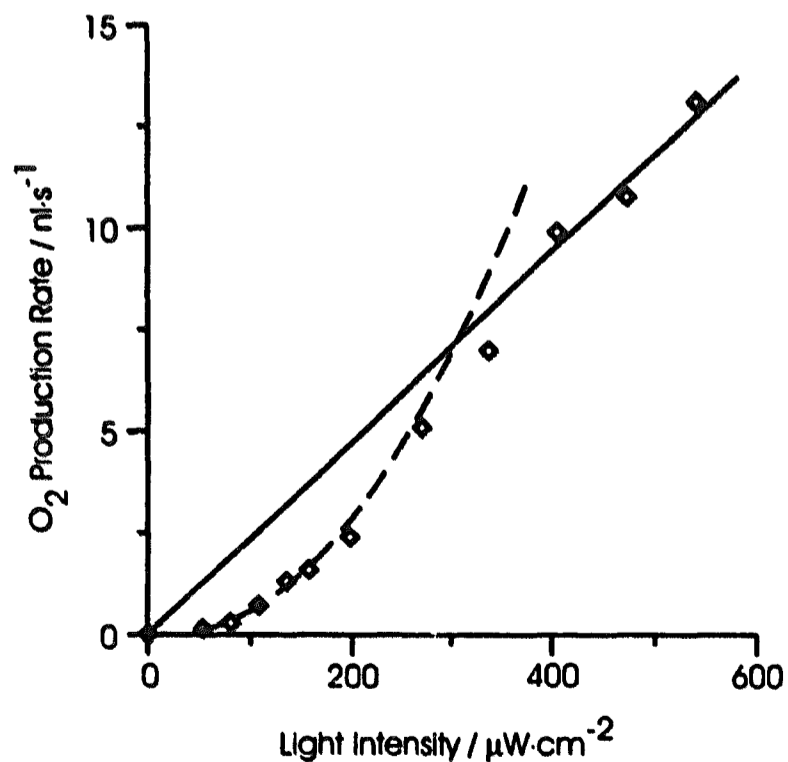


Fig. 5. O₂ evolution rate on AgCl/Ag⁺ layers on SnO₂-coated glass plates at various intensities of blue light (bandpass filter, 450 nm). Illuminated area: approximately 1 cm². Electrolyte: 0.1 M NaNO₃ with 10⁻³ M AgNO₃, pH 5.

changes to a linear dependence in the medium range. Much higher light intensities do not give meaningful results, because the samples are heated up and other artefacts may appear. We performed the same experiments with UV and green light and found the same behaviour. At low intensities, the O₂ evolution rate can be described as being proportional to the square of the light intensity. This non-linear dependence at low light intensity is not unexpected due to the four redox equivalents involved in the water oxidation process.

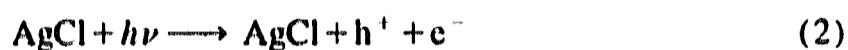
Up to now, we have hesitated to report a quantum yield for the photo-oxidation of water to O₂ because the parameters on which it depends were not well known. However, the quantum yield ϕ of photochemical O₂ evolution in the linear region of Fig. 5 can be evaluated because, in this experiment, the light intensity is directly proportional to the light absorbed by the AgCl/Ag⁺ layers on SnO₂-coated glass

$$\phi = \frac{\text{mol O}_2 \text{ per second} \times 4}{\text{mol photons absorbed per second}} \quad (1)$$

We have measured $\phi_{\text{UV}} \approx 0.8$, $\phi_{\text{blue}} \approx 0.8$ and $\phi_{\text{green}} \approx 0.5$, with an estimated error of 10%. This means that the four photons absorbed produce approximately 0.8 O₂ in the linear UV and blue ranges and approximately 0.5 O₂ in the linear green range. The estimated error is mainly due to uncertainties caused by reflectivity losses, which means that the values given are probably lower limits.

4. Mechanism of photochemical O₂ evolution

We now reflect on the mechanism of photochemical O₂ evolution described in the previous section, which should also explain the very different behaviour of AgCl/Ag⁺ and AgCl/Cl⁻, if possible. We symbolize the first step as a charge transfer absorption in which an electron-hole pair is formed



The electron-hole pair may recombine



or electrons and holes may separate and are finally trapped



The indices s and i refer to surface or interstitial species. We do not include luminescence, because the luminescence yield under these conditions is expected to be extremely low. Additional loss mechanisms to be considered are represented as

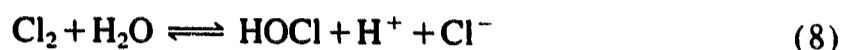


If the product species of reactions (4) and (5) live long enough, the trapped electrons and holes may react further. Surface chlorine radicals may react with each other and form molecular chlorine according to Eq. 7. The formation of OH[•]

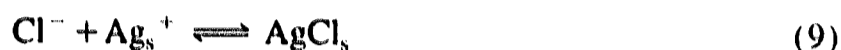
radicals was proposed in Ref. [8], but no evidence has been given so far for the formation of these very energy-rich species on near-UV or visible illumination; Cl₂ evolution has been measured in a number of different experiments [2,20–22,24]. We therefore believe that OH[•] is not formed under the conditions applied in our experiments.



Chlorine disproportionates according to



If this reaction plays a role, then it is important because it controls the concentration of free Cl⁻. Excess silver ions shift equilibrium (8) to the right because AgCl is formed



HOCl is a weak acid with a pK_a value of 7.58



Its acidic form is known to react in the dark in the presence of silver according to



whereas the hypochlorous anion OCl⁻ is stable under the same conditions. The photochemical activity of hypochlorous acid is well known. However, it does not play a determining role in our experiments because of insufficient absorption in the visible part of the spectrum. Eq. (7) explains why, with acidic conditions and an excess of Cl⁻, chlorine formation is observed, while Eq. (11) explains the oxygen evolution at Ag⁺ excess and medium pH. From a thermodynamic point of view chlorate and perchlorate are strongly favoured compared with hypochlorite, but due to kinetic reasons they are not formed at room temperature [23]. At high Cl⁻ concentrations, reaction (12) may also play a role



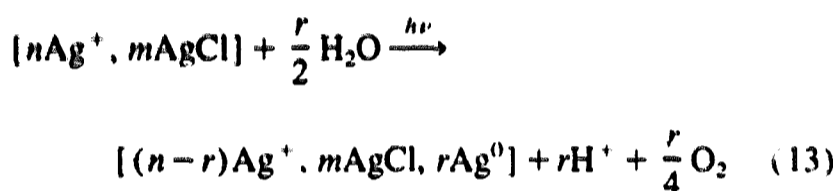
At low light intensities, we observed a non-linear dependence of the O₂ evolution rate on the light intensity which changes into a linear dependence at about 300 μW cm⁻². Four redox equivalents have to be accumulated for the formation of one O₂ molecule. In the mechanism presented, this occurs in steps (7) and (11), where two partially oxidized species react with each other. We assume that the recombination reaction plays a more important role at low light intensities than at higher values, because the speed of step (7) depends crucially on the Cl[•] concentration. The square dependence at low intensities is a hint that this reaction is second order with respect to the hole concentration symbolized as Cl[•]. The holes react rapidly to give Cl₂ in the linear range. Reactions (7)–(11) are consistent with all observations; however, direct evidence is missing.

The self-sensitization process of the water oxidizing ability of thin silver chloride layers on SnO₂-coated glass plates (Fig. 4) is assumed to be due to the same process as reported in earlier experiments [9,10,24]. New photoactive colour cen-

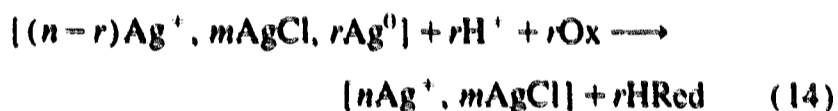
tres are formed on irradiation with UV light composed of reduced silver species. It appears that this process parallels what has become known as the Bequerel effect in silver halide photography [15].

5. Conclusions

We have found that thin silver chloride layers on SnO₂-coated glass plates evolve O₂ in the presence of a small excess of Ag⁺ ions in aqueous solution, with a maximum evolution rate at pH 4–5; this system shows the same type of self-sensitization of photochemical O₂ evolution as reported for Ag⁺-containing zeolite A systems. A non-linear dependence of the O₂ evolution rate on the light intensity at low intensities changes into a linear dependence in the medium range (above about 300 μW cm⁻²). The quantum yield per redox equivalent for O₂ evolution in the linear range is approximately 0.8 on UV and blue light illumination and approximately 0.5 in the green range. During the photo-oxidation of water, Ag⁺ is reduced according to the following stoichiometric equation which does not include the NO₃⁻ counter ions



The reduced silver species must be reoxidized to make the water oxidation useful for solar energy conversion. It is not difficult to find an oxidizing agent (Ox) which can oxidize the reduced silver according to



The dye bleaching photographic process is based on such a reaction. It is, however, more difficult to design a completely reversible system. Some possibilities have been discussed [10,25], and we are currently studying this in more detail.

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