141. Photoelectrochemistry with Colloidal Semiconductors; Laser Studies of Halide Oxidation in Colloidal Dispersions of TiO_2 and α-Fe_2O_3

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Summary

Aqueous sols of TiO_2 (anatase, particle radius 25 Å) were excited with (347.1 nm)-laser light and the reaction of valence-band holes with halide ions ($X = I^-$, Br^-, Cl^-) was investigated. Hole transfer takes place within the duration of the (10 ns)-laser pulse and results in the formation of anion radicals according to the sequence:

$$X^- \xrightarrow{h^+} X \cdot \xrightarrow{X^-} X_2^-$$
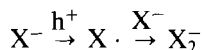
The quantum yield of X_2^- increases in the order $Cl_2^- < Br_2^- < I_2^-$, attaining 0.8 for I_2^- at pH 1. It is affected by pH, halide concentration and the presence of a protective agent for the sol.

RuO_2 deposited onto TiO_2 enhances markedly Cl_2^-- and Br_2^--formation, but has no effect on the yield of I_2^-.

Laser-photolysis investigation of halide oxidation were also carried out with colloidal Fe_2O_3 (particle radius 600 Å). For I_2-formation, the quantum yield exceeds 0.9 indicating almost quantitative hole scavenging by iodide.

Introduction. – In a series of recent investigations [1] we have demonstrated that colloidal semiconductors exhibit exceptionally high activity in artificial photosynthetic devices, producing fuels from visible light. Thus, ultrafine (50-100 Å)-sized particles of CdS or TiO_2, when loaded with appropriate catalysts, intervene as efficient mediators in the visible-light-induced cleavage of water [2] and hydrogen sulfide [3].

In order to elucidate the detailed mechanism of the photochemical events occurring in such systems, we have initiated laser-photolysis studies of interfacial electron-transfer process in colloidal semiconductor dispersions [4]. Moreover, the luminescence properties of CdS-particles have been exploited to study the nature of surface states and their annihilation by adsorbed species [4]. A kinetic model has also been conceived to analyze the dynamics of electron transfer and fluorescence events [5].

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In this communication, we pursue our studies on photoelectrochemical processes in colloidal semiconductor dispersions. The focus of our investigations is the reaction of valence-band holes of colloidal TiO_2 and Fe_2O_3 with adsorbed halide ions.

Experimental Part. – Colloidal solutions of TiO_2 were prepared by slowly adding 5 g of $TiCl_4$ (*Fluka, puriss.*) to 200 ml water at 0°. The solution was dialyzed until the pH reached a value around 3. A precise determination of the TiO_2-concentration was made by dissolving an aliquot of (10 ml)-solution (TiO_2-content = 5 g/l) in 20 ml conc. HCl-solution and refluxing for approx. 30 min. Subsequently, a Ti(IV)peroxo complex was formed by addition of 3 droplets of 30% H_2O_2-solution, which was spectro-photometrically analyzed [6] ($\lambda_{max} = 415$ nm, $\varepsilon_{max} = 640M^{-1}$ cm^{-1} in 6N HCl). The reference lightbeam was passed through a Ti(IV)-solution which had not been treated with H_2O_2.

At pH > 3 polyvinylalcohol (PVA) was used to stabilize the sol. Commercial PVA (*Mowiol* 98110, *Hoechst*, W. Germany) was pretreated in 5% aqueous solution by UV. light (450 W Xe-lamp, 4 h of irradiation to remove impurities that absorb 347.1 nm laser-light).

The size of the TiO_2-particles was determined by quasi-elastic light-scattering technique. The particle diameter derived from correlation functions was 50 Å. These particles consist mainly of anatase with a small proportion of amorphous material as shown by X-ray analysis.

Laser-photolysis experiments were performed with a frequency-doubled JK-2000 ruby laser. The (347.1 nm)-pulse had a duration of 10 ns and delivered 6.2×10^{16} photons. From the absorbance of the TiO_2-solutions (A = 1.3 at 347.1 nm and 0.5 g TiO_2/l) and the irradiated volume of the sample cell (0.03 cm³) one derives 4×10^{-5} Einstein/l for the absorbed photon concentration. Chemical actinometry with deoxygenated (methylviologen/TiO_2)-solutions at pH 8²) yielded for the absorbed photon concentration a value which was within 10% of this calculated value.

All materials employed were at least reagent grade. Dionized water was refluxed over alkaline permanganate and subsequently distilled twice from a quartz still.

Results and discussion. – 1. *Reaction of halide ions with TiO₂ valence-band holes.* The transient spectrum obtained immediately after the 347.1 nm laser excitation of colloidal TiO_2 (500 mg/l) in 0.5N HCl can be assigned to Cl_2^--radical ions [7] ($\lambda_{max} = 340$ nm, $\varepsilon_{max} = 8800 M^{-1}$ cm^{-1}³)). The formation of Cl_2^- can be rationalized in terms of band-gap excitation of the TiO_2-particle.

$$TiO_2 \overset{h\nu}{\to} TiO_2\,(e_{CB}^-, h^+) \tag{1}$$

generating conduction-band electrons (e_{CB}^-) and valence-band holes (h^+). The latter react with Cl⁻-ions to give (Cl ·)-radicals:

$$h^+ + Cl^- \to Cl \cdot \tag{2}$$

which subsequently undergo rapid complexation [7] by excess Cl⁻-ions

$$Cl \cdot + Cl^- \to Cl_2^- \tag{3}$$

²)   A detailed description of methylviologen reduction by conduction band electrons of TiO_2 is given in [4]. The quantum yield of this process at pH 8 is practically unity.

³)   This value of the extinction coefficient is based on a recent NBS-publication [7c]. For calculation of quantum yields we have employed $\varepsilon_{370} = 7000M^{-1}$ cm^{-1} [7c].

The prompt nature of Cl_2^--formation which occurs concomitantly and within the (10 ns)-laser pulse must be attributed to the fact that hole scavenging occurs predominantly by Cl^--ions that are adsorbed at the surface of TiO_2. If the hole-transfer *reaction 2* involved bulk diffusion of Cl^- towards the TiO_2-particle, then significantly longer reaction times would be required depending on Cl^--concentration. Surface-adsorbed species, on the other hand, can react extremely rapidly with photogenerated charge-carriers in colloidal semiconductors. In the case of a TiO_2-particle with a radius of 25 Å, the average transit time of a hole from the interior to the surface is calculated as only 1.2 ps [5] if the hole mobility is assumed to be equal to that of the electron. Thus, if interfacial charge transfer occurs promptly upon arrival of the charge carrier at the phase boundary, then oxidation of Cl^- is expected to occur in the picosecond-time domain.

Earlier photoelectrochemical studies with TiO_2-electrodes have shown [8] that holes readily react with water to produce oxygen:

$$4\,h^+ + 2\,H_2O \rightarrow 4\,H^+ + O_2 \qquad (4)$$

This process competes with chloride oxidation. In *Figure 1* is depicted the influence of pH on the Cl_2^--concentration determined at the end of the laser pulse. The Cl_2^--
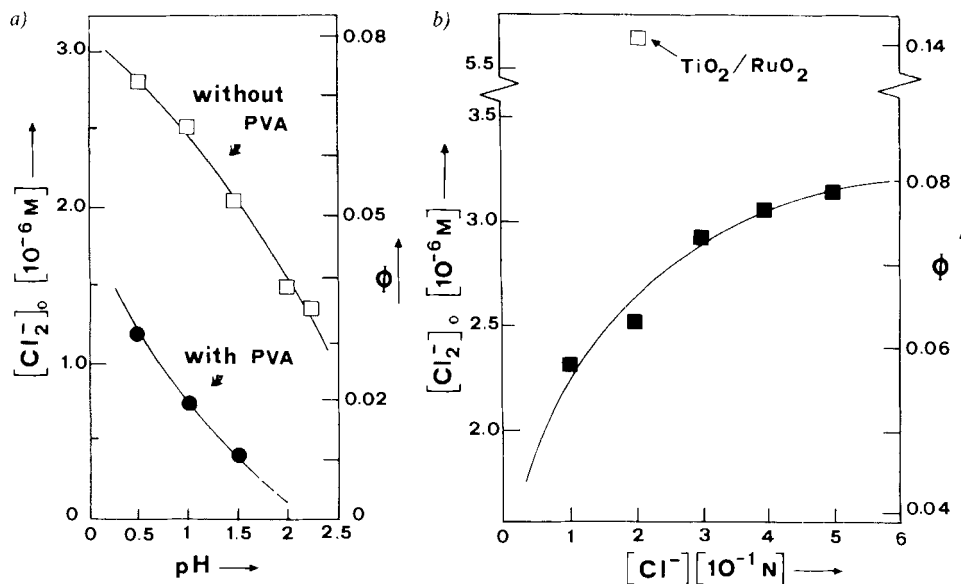

Fig. 1. *Laser photolysis of TiO_2-sol in the presence of chloride. a)* Effect of pH on the yield of Cl_2^- measured immediately after the laser pulse, $\varnothing$ represents the quantum yield for Cl_2^--formation, TiO_2]- = 500 mg/l, $[Cl^-] = 0.1\,N$, pH adjusted with $HNO_3/NaOH$, aerated solution.

□ Unprotected TiO_2-sol
● PVA (1 g/l) protected TiO_2-sol

b) Effect of Cl^--concentration on the yield of Cl_2^--formation pH = 1, concentration of Cl^- adjusted with NaCl (includes $0.1\,N$ HCl) unprotected sol, aerated solution.
■ The TiO_2-particles were loaded with 0.8% RuO_2 according to a previously published procedure [1c]

yield decreases sharply with increasing pH and is below detection limit at pH > 2.5. Apparently, at higher pH water oxidation is favored over that of Cl$^-$. This can be explained by thermodynamic arguments: for the (Cl$^-$/Cl$_2^-$)-couple, the standard potential ($E°$) is 2.3 V [9] and independent of pH. The first oxidation step of water

$$H_2O \rightarrow OH \cdot + H^+ + e^- \tag{5}$$

requires 2.2 V at pH 0 but the potential decreases by 59 mV/pH. As the valence-band potential of our colloidal TiO_2 shows the same pH-dependency [1c]

$$E_{VB}(TiO_2) = 3.07 - (0.059 \cdot pH) \tag{6}$$

the driving force of water oxidation is not affected, while that for Cl$^-$-oxidation decreases with increasing pH.

Figure 1 shows also that at a given pH, the Cl$_2^-$-yield is reduced by a factor of approximately two when PVA is introduced as a protective agent for the TiO_2-colloid. This polymer can apparently compete with H_2O and Cl$^-$ for valence-band holes. Nevertheless, it is surprising in view of the ease of oxidation of PVA, that Cl$_2^-$-formation is not completely surpressed in its presence. *Figure 1b* shows that the quantum yield of Cl$_2^-$-formation is also affected by Cl$^-$-concentration. At pH 1 an upper limit of Φ (Cl$_2^-$) = 0.08 is obtained when [Cl$^-$] $\geqslant$ 0.4 M.

Investigations analogous to those with Cl$^-$ were also carried out with Br$^-$ and I$^-$. The intermediates produced from the laser photolysis of colloidal TiO_2 in the presence of these halide ions are readily identified with Br$_2^-$- and I$_2^-$-radicals formed *via* the valence-band process *(Eqn. 7)*.

$$h^+ + X^- \rightarrow X \cdot \xrightarrow{X^-} X_2^- \ (X^- = Br^-, I^-) \tag{7}$$
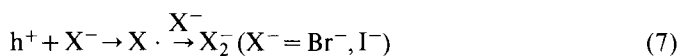
Figures 2 and 3 illustrate that the X$_2^-$-yield decreases sharply with increasing pH. At a given pH the quantum yield increases in the order Cl$_2^-$ > Br$_2^-$ > I$_2^-$. (The highest quantum yield measured for I$_2^-$ at pH 1 is 0.8, indicating that 80% of the holes produced by the laser flash in the colloidal semiconductor are scavenged by iodide). It should be noted that this sequence is related to the redox potentials[4] in that $E°$(Cl$^-$/Cl$_2^-$) = 2.3 V > $E°$(Br$^-$/Br$_2^-$) = 1.7 V > $E°$(I$^-$/I$_2^-$) = 1.0 V [9]. Apart from the driving force, the effect of pH reflects also coulombic interactions since the particle charge changes from positive to negative at pH > 3.3 [1c] (point of zero zeta-potential of TiO_2-particles of similar size). Note that for all halide ions the yield of oxidation is comparatively small at pH > 3.5 indicating repulsion of X$^-$ from the TiO_2-surface.

Figure 4 shows that the quantum yield of X$_2^-$-formation increases with concentration of halide ions. The experimental curves display a *Langmuir*-absorption isotherm type behavior as was found for Cl$^-$-ions. This finding amplifies our earlier

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[4]   *Herrmann & Pichat* [10] have investigated the oxidation of halide ions by oxygen in irradiated TiO_2-dispersions. No oxidation of Cl$^-$ was observed. The quantum yield for I$^-$-oxidation (2%) was 80 times that for Br$^-$-oxidation.

conclusion that only halide ions adsorbed to the surface of TiO_2 can intervene as hole scavengers.

The effect of protective agent concentration on the yield of Br_2^- is illustrated in *Figure 5*. Surprisingly, after an initial decrease by a factor of two the quantum yield of Br_2^--formation increases slightly with PVA-concentration until a plateau is attained. This shows that the intervention of PVA as a hole scavenger is rather inefficient even at high surface coverage of the TiO_2-particle.

2. *Effect of RuO_2 on the quantum efficiency of halide oxidation.* RuO_2 is known to be an electrocatalyst for both, the oxidation of water and halide ions [11]. Dimen-
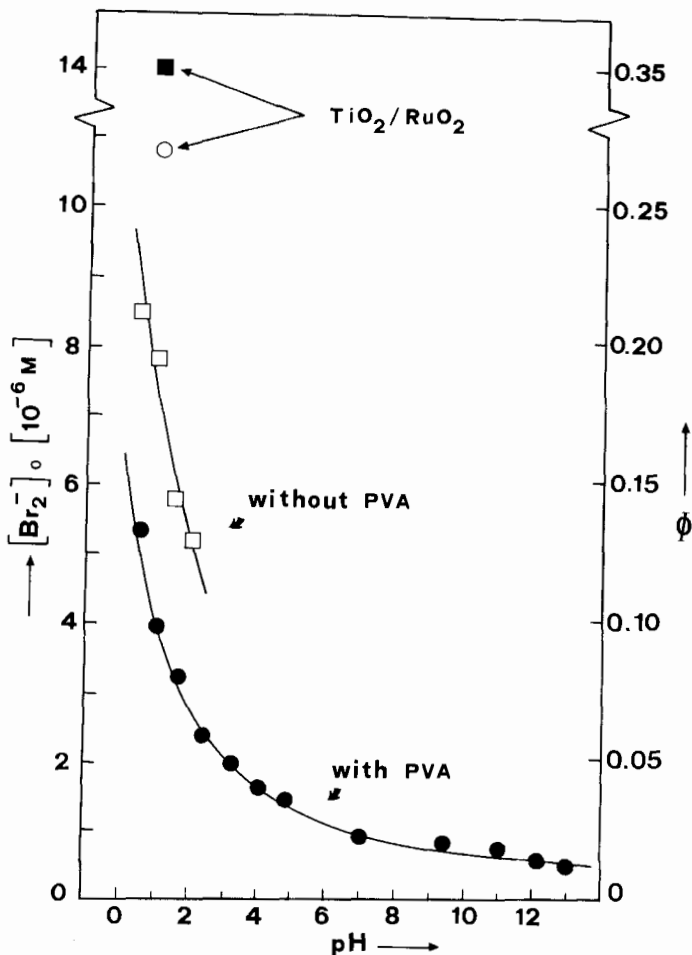

Fig. 2. *Laser photolysis of colloidal TiO_2 in the presence of bromide, effect of pH on the quantum yield of Br_2^--formation* ([Br^-]=0.2 N, pH adjusted with $NaOH/HNO_3$, aerated solution)

□ Unprotected sol.
■ Unprotected sol loaded with 0.8% RuO_2.
● PVA (1 g/l)-protected sol.
○ PVA (1 g/l)-protected sold loaded with 0.8% RuO_2.

sionally stable RuO_2-anodes have been employed in industrial chloride-electrolysis. Our previous studied have shown that RuO_2-deposits on CdS-[2], TiO_2-[1] or WO_3-[12] powders enhance hole transfer from the valence band of the particle to water resulting in oxygen generation.

Figures 1, 2 and 3 show the influence of RuO_2-deposits on TiO_2-particles on the reaction of halide ions with $h^+(TiO_2)$. A pronounced increase in the quantum
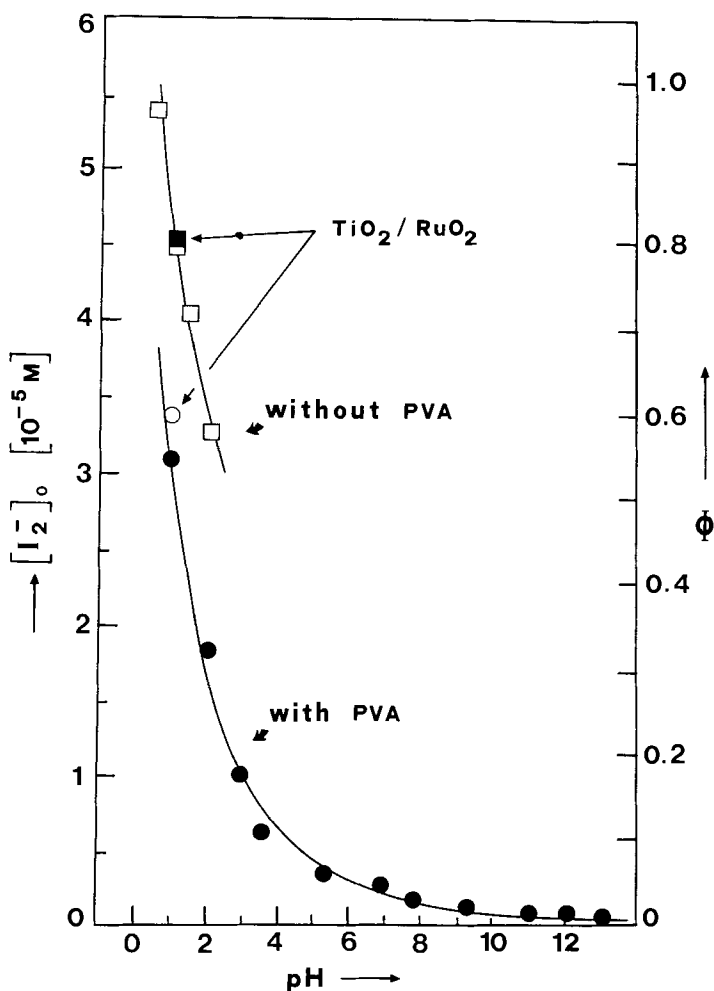

Fig. 3. *Laser photolysis of colloidal TiO₂ in the presence of iodide, effect of pH on the quantum yield of I₂⁻-formation, aerated solutions* ([I⁻] = 0.2 N, [TiO₂] = 500 mg/l, pH adjusted with HClO₄/NaOH; concentrations of I₂⁻ were calculated using an extinction coefficient of $\varepsilon_{390} = 1.4 \times 10^4 M^{-1} cm^{-1}$ [18]. Higher and smaller ε values have also been reported [7e])

● PVA (1 g/l) protected sol, no RuO_2
○ PVA (1 g/l) protected sol, loaded with RuO_2(0.8%)
□ Unprotected sol without RuO_2
■ Unprotected sol with RuO_2

efficiency of Cl_2^-- and Br_2^--generation is observed while the I_2^--formation is not affected. For Cl_2^- the enhancement is 2.25 fold and for Br_2^- it is 2.7 or 1.8 fold in solutions with and without PVA, respectively.

These results illustrate a pronounced catalytic effect of RuO_2 on the oxidation of chloride and bromide ions by TiO_2-valence band holes. In contrast, for iodide no catalysis is observed. Apparently, in the latter case the driving force for the reaction is high enough to insure very efficient hole transfer even in the absence of RuO_2 deposits.

3. *Light-induced halide oxidation by colloidal Fe_2O_3.* We wish to report some preliminary experiments with a-Fe_2O_3-sols[5]). These colloidal dispersions exhibit an absorption band rising steeply towards the UV. below 600 nm, which coincides with the 2.2 eV band-gap of crystalline a-Fe_2O_3. Laser experiments were performed with solutions containing 20 mg Fe_2O_3/l. (At this concentration, the absorbance at 347.1 nm is identical with that of 500 mg/l TiO_2-sol). Iodide (0.2 M, pH 1) was employed as a hole scavenger. Laser excitation of Fe_2O_3-particles under these conditions leads to extremely rapid (~ 10 ns) formation of I_2^-. The quantum yield of I_2^--formation is surprisingly high and amounts to more than 80%. In a subsequent reaction I_2^- disappears according to a second-order rate law with a specific rate of

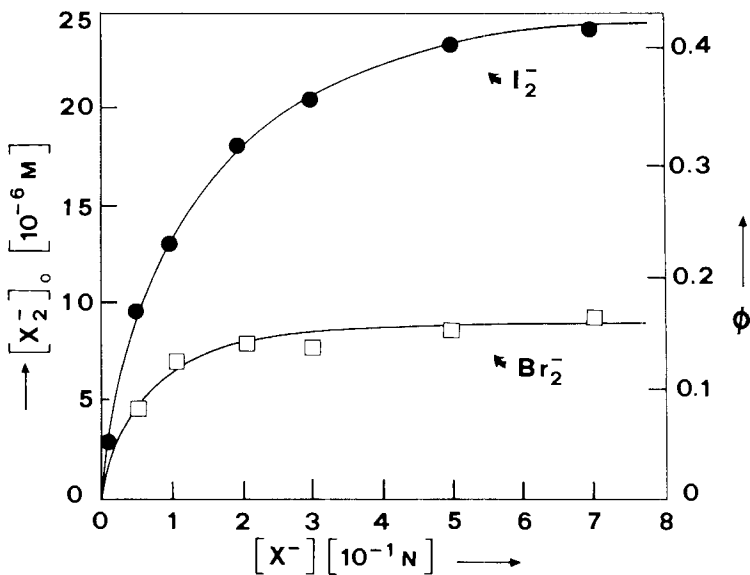Fig. 4. *Effect of halide concentration on the yield of Br_2^- and I_2^- measured immediately after laser excitation of colloidal TiO_2(500 mg/l)*

☐ Br^-, concentration adjusted with NaBr, pH 0.5 (adjusted with HNO_3), PVA (1 g/l)-protected sols.
● I^-, concentration adjusted with NaI, pH = 2 (adjusted with $HClO_4$), PVA (1 g/l)-protected sols.

5)   These a-Fe_2O_3-sols were kindly supplied by Dr. *Eisenlauer, BASF,* Ludwigshafen, West Germany, Their hydrodynamic radius is 600 Å.
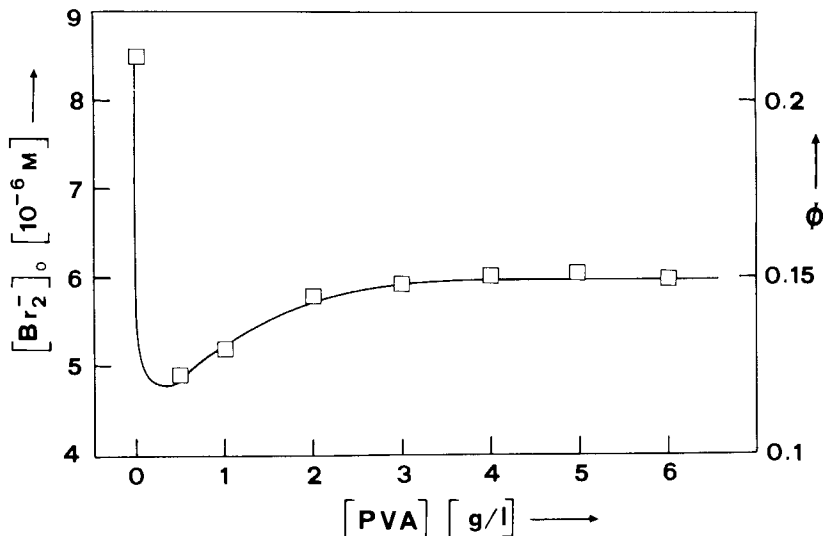
Fig. 5. *Effect of protective agent concentration on the yield of Br_2^-, measured immediately after laser exposure of colloidal TiO_2 (500 mg/l) ([Br$^-$]= 0.2N, pH 0.5 (adjusted with HNO$_3$) aerated solutions)*

$k = 7 \times 10^9 \, \text{M}^{-1}\text{s}^{-1}$. A similar decay was observed for the halide radical ions in the TiO_2-dispersions. It is attributed to the diffusion-controlled dismutation reaction

$$2\,X_2^- \rightarrow X_2 + 2\,X^- \tag{8}$$

The fact that photogenerated holes in Fe_2O_3-particles can be scavenged with high efficiency by electron-donors such as iodide is important with regard to the use of such particles in solar-energy-conversion devices. Single crystal [13] and polycrystalline [14] a-Fe_2O_3-electrodes show disappointingly small efficiences as photo anodes for the oxidation of water and other substrates. This arises from the low mobility of charges carriers [15] ($\sim 0.1 \, \text{cm}^2 \, \text{V}^{-1}\text{s}^{-1}$), a short hole-diffusion length (20-40 Å) [16]) and fast surface recombination [17]. The advantage of employing Fe_2O_3-sols is that the particle dimension can be reduced to a size where practically all the photo-induced charge carriers attain the particle surface before recombination can occur. In this context, our recent finding of efficient oxygen generation by visible light in colloidal Fe_2O_3-dispersions is particularly encouraging. Such systems are suitable to become the oxygen-producing part in a complete water cleavage system.

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