Time-Resolved Rise of I_2^- upon Oxidation of Iodide at Aqueous TiO_2 Colloid

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The rise of the one-electron oxidation intermediate I_2^- formed upon band-gap excitation of bare TiO_2 colloidal particles in aqueous iodide solution has been resolved for the first time. These measurements are based on a very sensitive transient absorption technique that allows monitoring of I_2^- at iodide concentrations as low as 10^{-4} M. The linear dependence of the pseudo-first-order rise constant on iodide concentration (slope = $(7.9 \pm 1.2) \times 10^9$ L mol^{-1} s^{-1}) suggests that the observed step reflects the reaction of surface-adsorbed I atoms with iodide from the surrounding solution phase. The adsorbed I atoms are formed by the reaction of surface-adsorbed iodide with valence band holes within the 5-ns duration of the 355 band-gap excitation pulse. Analysis of the decay kinetics of I_2^- and measurement of the concurrent I_3^- yield revealed that interparticle reduction by trapped conduction band electrons is the main decay path of I_2^-. These results are compared with a previous time-resolved study of iodide photooxidation at dye-sensitized TiO_2 colloids.

I. Introduction

Oxidation of halides, especially iodide, at TiO_2 electrodes in photodriven electrochemical cells has recently proved very promising for light-to-electrical energy conversion.[1-4] By loading high-surface-area films of the semiconductor (band-gap 3.2 eV) with visible and near-infrared light-absorbing dyes, a match between the optical absorption profile of the electrode and the solar spectrum can be achieved. Improvement of the solar-to-electrical energy conversion efficiency of halide/halogen regenerative photoelectrochemical cells hinges mainly on a more effective tapping of the abundant red and near-infrared solar photons.[5] Since the driving force for halide oxidation sensitized by long-wavelength visible and near-infrared light is small, a detailed knowledge of elementary redox steps at the semiconductor–solution interface is crucial. This would furnish the basis for optimization of the rate of each redox step and hence of the overall conversion efficiency.

Flash photolytic studies of halide oxidation at TiO_2 were first conducted on bare colloidal particles by the groups of Grätzel[6] and Henglein,[7] and subsequently by Fox.[8] In the time-resolved study by Fox, iodide oxidation was also monitored at TiO_2 powders.[8] The one-electron oxidation intermediate I_2^- (Br_2^-, Cl_2^-) was found to be formed in each of these studies, and its kinetics was monitored by the $^2\Sigma_g^+ \leftarrow {}^2\Sigma_u^+$ absorption in the near-UV region.[9] The rise of the intermediate was found to be complete within the 10–30-ns width of the 350-nm band-gap excitation pulse even at the lowest halide concentration used (0.01 M).[6-8] The elementary reaction steps involved in the formation of I_2^- (Br_2^-, Cl_2^-) could therefore not be studied by the methods employed in these earlier works.

Using a very sensitive transient absorption technique for monitoring of the $^2\pi_g \leftarrow {}^2\Sigma_u^+$ transition[9] of I_2^- in the near-infrared region, we have recently been able to resolve for the first time the rise of this one-electron oxidation intermediate at dye-sensitized TiO_2 colloidal particles.[10] The sensitizer employed was phenylfluorone (2,6,7-trihydroxy-9-phenylisoxanthen-3-one, ethanolic sol). The observed rise of I_2^- was attributed to the reaction of transient I atoms adsorbed on the TiO_2 surface with I^- from the surrounding solution. Since the efficiency of I^- oxidation at the phenylfluorone-sensitized TiO_2 colloid was determined to be much lower than the corresponding photoelectrochemical efficiency at a PF/TiO_2 polycrystalline electrode,[11] an additional process, namely, recapture of photoinjected conduction band electrons by adsorbed I atoms, was proposed to limit the I_2^- yield. By contrast, RuL_3-sensitized TiO_2 colloid particles (RuL_3 = tris(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) dichloride, aqueous sol) gave rise to a transient that had significantly different absorption cross section and kinetics than I_2^-. The species was assigned as a $RuL_3I_2^-$ ion pair that preceded formation of free I_2^-.[10]

An important next step in advancing our understanding of the sensitizer dependence of the primary processes of I^- oxidation at TiO_2 colloids is the elucidation of the reactive events leading to the formation of I_2^- at bare TiO_2 particles. The results of these measurements, including a detailed study of the fate of I_2^- in aqueous TiO_2 sols, are reported here.

II. Experimental Section

For time-resolved absorption measurements, a tunable cw dye laser (Coherent Model 599-01, pumped by an Ar ion laser Coherent Model Innova 90-5) was used as a probe source in conjunction with a pulsed Nd:YAG photolysis laser (Quanta Ray Model DCR-2A). This system was described in detail in a previous report.[12] Samples contained in a 1-cm quartz cell were irradiated at 355 nm with pulses of 5-ns duration (1 Hz). The pulse energy was measured with a Gentech Joule meter and corrected for reflection loss at the cell. Transient absorption was measured perpendicular to the photolysis laser beam. The dual-beam cw dye probe laser system with a tuning range from 460 to 1000 nm featured one or the other of two differential photodiode detectors (DPDs). One differential detector was equipped with two United Detector Technology silicon photodiodes Model PIN-10D. The detector circuit was configured to generate a voltage proportional to the difference of intensity of the light incident on the two photodiodes. The rise time of the signal output of this detector was 35 ns. The second differential detector was equipped

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with two Hamamatsu silicon photodiodes Model 1722-01. With a fast-response differential circuit, the rise time of this detector was measured as 8 ns. The photodiodes were protected against scattered pump laser light by optical filters (Schott Glass Model 0G 570). The signal was amplified and digitized by a LeCroy data acquisition system (digitizers Models TR8818 and 6880). Typical absorbance detection limit in the 600–800-nm region was 1×10^{-5} absorbance units (au) (35 ns rise time detector, 400 laser pulse average). Laser dyes used to cover this range were Rhodamine 590, DCM, and LDS 721 (Exciton).

Static UV–vis spectra were measured by a Hewlett-Packard diode array spectrometer Model 8452 or a Shimadzu Model UV-2100 spectrometer.

Aqueous TiO_2 colloid was prepared according to procedures described in the literature.[13] The mean particle diameter as determined by electron microscopy and quasi-elastic light scattering was 11 nm. A Raman spectrum of the above TiO_2 particles agreed with that of anatase. The stock solution contained 6 g/L TiO_2 at pH = 2.2. Experiments under acidic conditions were normally performed with solution diluted to give 1 g/L TiO_2 at pH = 2.7. Studies under basic conditions were performed using 1 g/L TiO_2 sols at pH = 12.0. These colloids were prepared by mixing rapidly a solution containing 2 g/L TiO_2 (pH = 2.5) with an equal volume of 0.036 M aqueous NaOH. No stabilizing polymers were introduced in any of the colloidal solutions.

For preparation of a colloidal TiO_2 suspension in glycerol, $Ti^{IV}(OC_2H_5)_4$ (10 mL, Alfa) was added dropwise to 150 mL of methanol, acidified by 0.5 mL of concentrated $HClO_4$, and cooled to 0 °C. The opaque suspension was stirred for 1 h to completely dissolve the titannic polymer chains. The clear solution was recooled to 0 °C, and 3 mL of water was added. After stirring for 3 h at room temperature, the light yellow color disappeared completely. The colorless methanolic colloid, which consisted mainly of amorphous TiO_2, was refluxed for 90 h. The concentration of the TiO_2 was determined gravimetrically at 40 g/L. Quasi-elastic light scattering indicated a hydrodynamic particle diameter of about 13 nm. The final solution was obtained by diluting 10 mL of methanolic colloid with 90 mL of glycerol.

Potassium iodide (Fisher Scientific) was added to the colloid in the form of a concentrated aqueous solution. Stock solutions were adjusted to give the desired KI concentration in the resulting colloidal dispersion upon addition of a volume equal to 1% of the volume of the sol. Water used to prepare solutions was distilled and passed through Millipore columns for further purification.

III. Results

1. Time-Resolved Rise of I_2^-. UV-visible spectra of aqueous TiO_2 sols showed the well-known band-gap absorption with an onset around 380 nm.[14] Band-gap excitation of the colloidal solution at 355 nm resulted in the familiar broad absorption of trapped conduction band electrons at red and near-infrared wavelengths.[15-17] We calculate that seven electron-hole pairs were generated per TiO_2 particle under the following experimental conditions; particle concentration, 6×10^{-7} M (1 g of TiO_2/L); absorbance at 355 nm, 0.57; pulse energy, 2.0 mJ; irradiation volume, 1 cm^3. The main part of the transient absorption signal of the trapped electrons decayed within less than 100 ns, with a weak tail extending into the millisecond time range. The initial fast decrease of the trapped electron concentration is due to recombination with free valence band holes. The slow decay is assigned to reaction of trapped electrons with trapped holes.[15]

Figure 1a shows the transient absorption at 700 nm observed upon 355-nm excitation (2 mJ $pulse^{-1}$) of the aqueous TiO_2 sol described above (6×10^{-7} M, pH = 2.7) but now with 0.02 M KI added. This transient is assigned to I_2^- based on previous I^- photooxidation studies at bare TiO_2 colloid by Grätzel,[6] Henglein,[7] and Fox.[8] The spectrum of the transient, shown in Figure 1b, has a peak at 750 nm, consistent with the $^2\pi_g \leftarrow {}^2\Sigma_u^+$ absorption

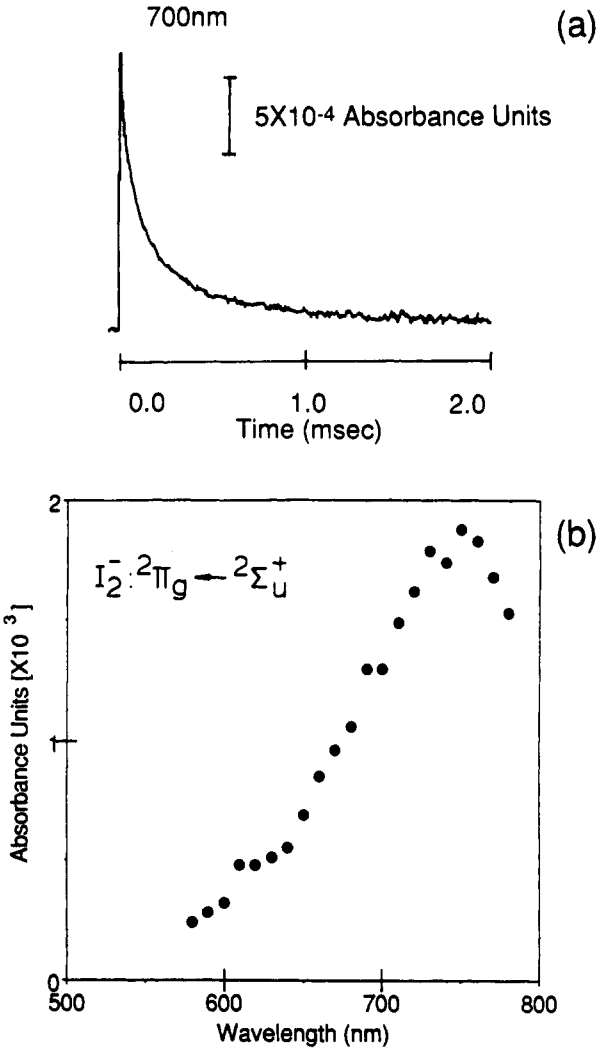

Figure 1. (a) Transient absorption at 700 nm following 355-nm (2 mJ $pulse^{-1}$) excitation of aqueous TiO_2 sol (1 g/L) at pH = 2.7 containing 0.02 M KI. (b) Spectrum of the transient.

of I_2^-.[9,10,18] If, however, I_2^- were the only species absorbing in this region, we would expect an absorbance of 1.1×10^{-4} at 600 nm based on the observed absorbance of 1.8×10^{-3} at the 750-nm peak. Instead, the measured absorbance at 600 nm is significantly larger, namely, 3.0×10^{-4}. The additional absorption at 600 nm is most probably due to trapped conduction band electrons.

By virtue of the high sensitivity of the cw dye laser based absorption spectrometer, we were able to monitor the I_2^- signal at iodide concentrations as low as 10^{-4} M. This allowed us to resolve for the first time the rise of I_2^- produced upon oxidation of I^- at unsensitized TiO_2 particles. Figure 2a shows the rise of the intermediate at 730 nm for $[I^-]$ in the range from 2.5×10^{-4} to 10^{-2} M (355-nm excitation, 2 mJ cm^{-2}, particle concentration 6×10^{-7} M, pH = 2.7). The signals were measured with the 35-ns response time differential photodiode detector. While the rise of the intermediate for $10^{-4} < [I^-] < 10^{-3}$ M was much slower than the detector response, the I_2^- signal for $[I^-] = 10^{-2}$ M is clearly limited by the 35-ns detector response. This was confirmed by measurement of the I_2^- rise in a 10^{-2} M iodide sol with the fast (8-ns) photodiode detector. As can be seen from Figure 2b, the 1/e rise is around 10 ns. A plot of the 1/e rise time of the I_2^- absorption vs $[I^-]$, Figure 3, shows that these pseudo-first-order rise constants depend linearly on the iodide concentration. The corresponding bimolecular rise constant is $(7.9 \pm 1.2) \times 10^9$ L mol^{-1} s^{-1}.

2. Decay of I_2^-. Figure 4a shows static UV difference spectra taken at regular intervals upon 355-nm irradiation of an air-saturated aqueous TiO_2 colloid (6×10^{-7} M, pH = 2.7) containing

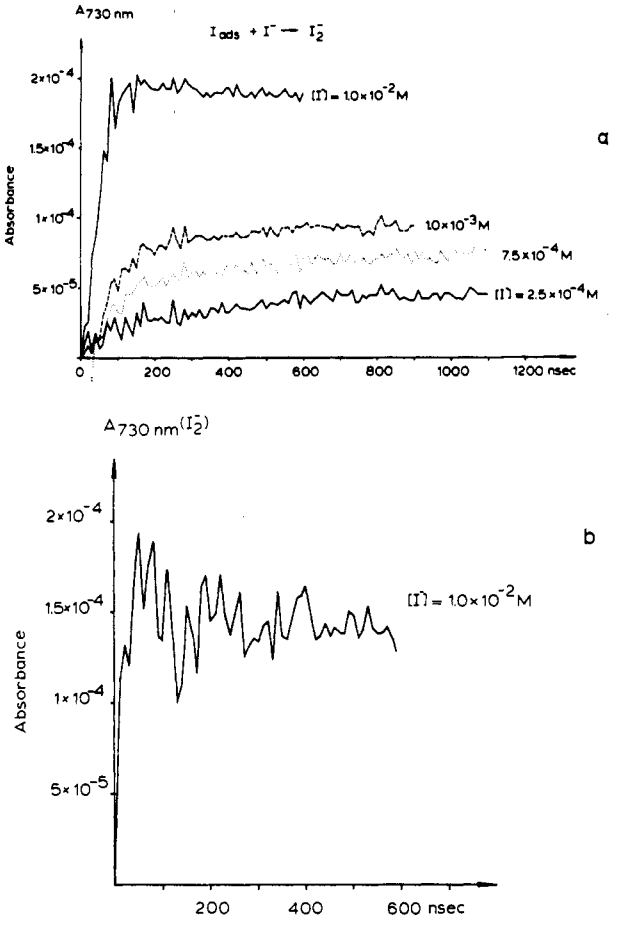

Figure 2. (a) Transient absorption at 730 nm following 355-nm (2 mJ pulse $^{-1}$) excitation of aqueous TiO_2 colloid (1 g/L) at pH = 2.7 containing KI at the concentrations indicated. Measurements were made with the 35-ns DPD detector. (b) Measurement at $[I^-] = 10^{-2}$ M with the 8-ns response-time DPD.

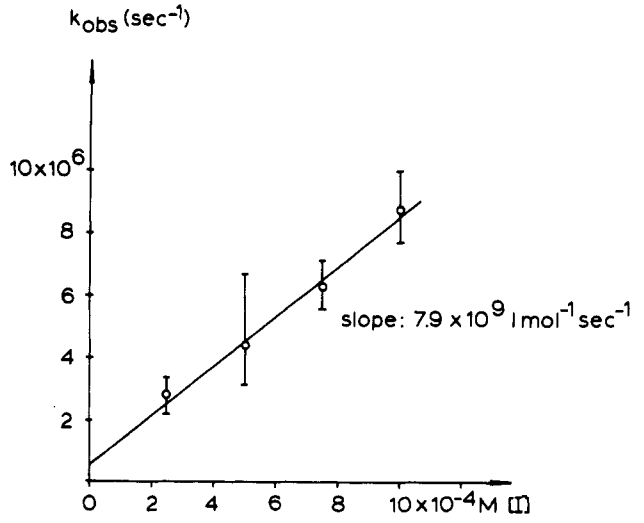

Figure 3. Pseudo-first-order rate constant of the rise of the I_2 absorption as a function of iodide concentration.

0.02 M I^-. Spectra recorded after 500, 1000, and 1500 excitation pulses agree well with that of I_3^-.[19] Moreover, Figure 4a shows that the yield of I_3^- is linear in 355-nm exposure even after as many as 1500 laser shots. Averages of transient I_2^- signals taken after 500, 1000, and 1500 laser pulses are also unchanged as can be seen in Figure 4b. Hence, the yield of I_3^- based on I_2^- remains constant upon prolonged 355-nm irradiation. This indicates that there is no secondary chemistry of accumulated I_3^- that would reduce the I_3^- buildup such as reduction by trapped conduction band electrons. We can readily determine the efficiency of I_3^-

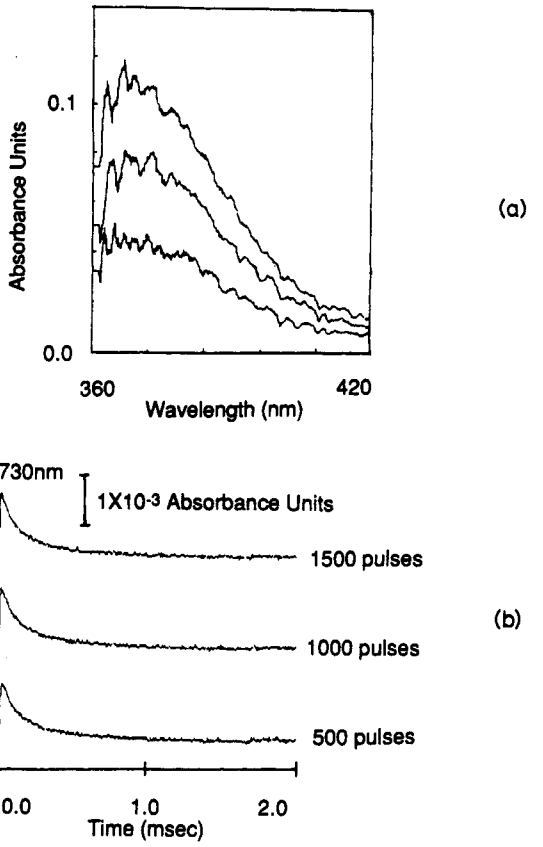

Figure 4. (a) Static UV–visible absorption spectra measured following excitation of TiO_2 colloid (1 g/L, pH = 2.7) containing 0.02 M I^- by 500, 1000, and 1500 laser pulses at 355 nm (2 mJ pulse^{-1}). The spectrum of the TiO_2 sol before irradiation has been subtracted. The noise at $\lambda <$ 400 nm originates from subtraction of the strong TiO_2 absorption.

production by the disproportionation reaction

$$I_2^- + I_2^- \rightarrow I_3^- + I^- \quad (1)$$

on the basis of the data presented in Figure 4. From the transient I_2^- signal after 500 laser pulses, Figure 4b, and $\epsilon(I_2^-, 730\text{ nm}) = 2700$ L mol^{-1} cm^{-1},[18] we calculate an I_2^- yield of 4.7×10^{-7} M per laser pulse, hence, a concentration of 2.3×10^{-4} M after 500 pulses. According to the stoichiometry of reaction 1, 1.2×10^{-4} M I_3^- would be produced if the reaction yield were unity. Since the ratio of the total solution volume to the irradiated volume is 3.0 and the concentrations equilibrate prior to recording of a UV spectrum, an I_3^- absorbance growth at 360 nm of 1.04 would be expected after 500 laser pulses ($\epsilon(I_3^-, 360\text{ nm}) = 26\,000$ L mol^{-1} cm^{-1}).[19] The observed growth is 0.04 au; hence, the yield of reaction 1 is only 4%. We conclude that the disproportionation reaction (1) is only a minor decay path of I_2^-.

There are two additional observations that corroborate this conclusion. First, it has been established in previous flash-kinetic studies with band-gap-irradiated bare TiO_2 particles that reaction of valence band holes with electron donors results in formation of long-lived (millisecond) trapped conduction band electrons.[15,16,20] Hence, every reactive event according to eq 1 is expected to leave behind two long-lived electrons. Since the latter also absorb at 730 nm, the residual absorbance after 2-ms decay of the signal, Figure 4b, would furnish an upper limit for the concentration of trapped electrons per photolysis laser pulse. With $\epsilon^{cb}(730\text{ nm}) = 960$ L mol^{-1} cm^{-1} and a residual absorbance of 8×10^{-5} au, we calculate an upper limit of 8×10^{-8} M for the trapped electron concentration. This constitutes at the same time an upper limit for I_2^- loss per pulse due to disproportionation (eq 1). Hence, on the basis of this estimate, we expect after 500 laser pulses an I_3^- buildup of at most 6.7×10^{-6} M, giving rise to an absorbance of 0.17 at 360 nm. This falls far behind the I_3^- growth

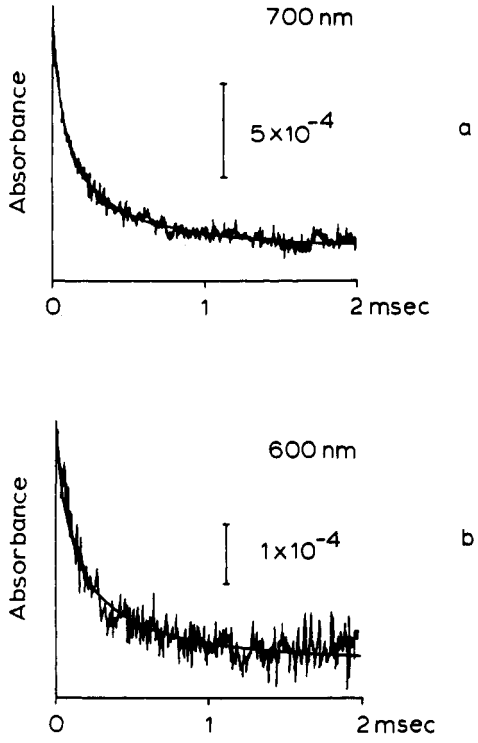

Figure 5. Transient absorbance decay following 355-nm (2 mJ pulse^{-1}) excitation of aqueous TiO_2 colloid (6×10^{-7} M, pH = 2.7) containing 0.02 M KI. (a) Decay at 700 nm. (b) Decay at 600 nm. The solid traces indicate fits of the second-order law describing reaction 2.

of 1.04 au calculated assuming that decay of I_2^- occurs exclusively by disproportionation (eq 1) (see preceding paragraph). Second, the decay constant of 1.8×10^{10} L mol^{-1} s^{-1} obtained by fitting the second-order rate law corresponding to reaction 1 to the curves shown in Figure 4b does not agree with the established rate constant of I_2^- disproportionation in aqueous solution (8×10^9 L mol^{-1} s^{-1}).[21] It is important to add that in their recent time-resolved study of I^- photooxidation at bare aqueous TiO_2 colloid, Draper and Fox[8] also observed only a very small I_3^- buildup per laser pulse when monitoring transient absorption in the 360–500-nm region. Taking into account the extinction coefficients of I_3^-(360 nm) = 26 000 L mol^{-1} cm^{-1} [19] and I_2^-(400 nm) = 14 000 L mol^{-1} cm^{-1},[22] one obtains from a spectrum taken 155 μs after the 355-nm laser excitation flash an I_3^- yield of at most 6% based on I_2^- (t = 0) (Figure 1 of ref 8).

The only alternative decay pathway of I_2^- we can think of is reduction by trapped conduction band electrons

$$I_2^- + e^-_{cb} \rightarrow I^- + I^- \qquad (2)$$

Since one trapped electron is formed for every I_2^- produced, the decay of I_2^- would follow the simple second-order rate law of a single reactant.[23] The rate constant can be derived from the measured absorbance decays by using $c^{I_2^-} = c^{cb} = A/l(\epsilon^{I_2^-} + \epsilon^{cb})$ (c, concentration; A, measured absorbance; l, path length of the probe beam; $\epsilon^{I_2^-}$ and ϵ^{cb}, extinction coefficients of I_2^- and trapped electrons at the probe wavelength). Parts a and b of Figure 5 show transient absorbance decays at 700 and 600 nm, respectively, upon 355-nm excitation of a TiO_2 sol containing 0.02 M KI. Using $\epsilon^{I_2^-}$(700 nm) = 2200 L mol^{-1} cm^{-1} [18] and ϵ^{cb}(700 nm) = 1040 L mol^{-1} cm^{-1},[17] a rate constant of 2.6×10^{10} L mol^{-1} s^{-1} was derived for reaction 2 from a fit of the absorbance decay curve in Figure 5a. The calculation, which neglects the loss of I_2^- by process 1, was performed using the Gauss–Newton iterative method described in a previous paper.[12] Similarly, a rate constant of 3.0×10^{10} L mol^{-1} s^{-1} was obtained from a fit of the decay at 600 nm, Figure 5b ($\epsilon^{I_2^-}$ (600 nm) = 220 L mol^{-1} cm^{-1}, ϵ^{cb}(600 nm) = 1200 L mol^{-1} cm^{-1}).[17,18] The good agreement of the fits (Figure 5) and of the rate constants at the two probe wavelengths strongly supports our interpretation of the near-infrared absorbance decay in terms of reaction 2. The rate constant also agrees well with the 3×10^{10} L mol^{-1} s^{-1} decay constant obtained by Draper and Fox when monitoring the I_2^- decay at 400 nm.[8] It is important to note that a kinetic analysis of the signal decay in the 400-nm region alone does not allow distinction between reactions 1 and 2 because both follow a simple second-order rate law (the absorption cross section of trapped conduction band electrons at 400 nm is about 50 times smaller than that of I_2^- [17,22]).

The second-order rate constant was found to be unaffected even by as much as a 4-fold change of the initial concentration of I_2^- and e^-_{cb} (by varying the 355-nm excitation pulse energy). Similarly, a 10-fold variation of the TiO_2 particle concentration (0.6–6.0 g/L) did not have any effect on the second-order decay constant, consistent with the attribution of the I_2^- decay to process 2. In these experiments, the pH was kept at 2.7 and [I^-] at 0.02 M. On the other hand, a change of the pH had a pronounced effect on the I_2^- decay kinetics. We found that the decay rate constant increased by a factor 1.66 when raising the pH from 1.06 to 2.02.

Similar transient absorption experiments were conducted with TiO_2 colloidal particles suspended in a "glycerol" solution (90% (vol) glycerol, 10% methanol). The purpose of this was to try to distinguish between intra- and interparticle quenching of I_2^- by trapped electrons (process 2). Particle concentration was 6×10^{-7} M, and the pH was adjusted to 2.5 using perchloric acid. In the absence of KI, excitation at 355 nm resulted in a long-lived transient absorption in the near-infrared (measured at 725 nm) whose decay time was limited by the 25-ms measurement limit of the acquisition electronics. The signal is attributed to trapped conduction band electrons whose long lifetime originates from the fact that the photogenerated holes are efficiently reduced by the organic solvent.[20,24] Excitation at 355 nm of the sol after addition of KI to give a 0.05 M I^- solution resulted in I_2^- transient absorption. Although the yield of I_2^- was over an order of magnitude smaller than that observed in the aqueous TiO_2 colloid, the decay time could readily be determined and was also found to be limited by the 25-ms measurement range of our system. We calculate that the bimolecular decay constant of I_2^- must therefore be smaller than 5×10^8 L mol^{-1} s^{-1}.

3. I_2^- Yield as a Function of pH and I^- Concentration. Experiments were performed at high pH to examine the effect of the TiO_2 surface charge on the efficiency of I^- oxidation. Colloidal TiO_2 particles carry a positive charge in acidic solution but a negative charge in basic solution.[14,25,26] Hence, in acidic solution, the particles will adsorb I^- due to electrostatic attraction, while at high pH I^- adsorption is expected to be negligible. When exciting a basic (pH = 12) TiO_2 sol at 355 nm in the absence of KI, a very broad transient absorption with a maximum around 800 nm was observed which is assigned to trapped conduction band electrons. The shift of this band to longer wavelengths when compared with acidic sols has previously been noted by Grätzel and co-workers.[17] Upon addition of 0.01 M I^-, no change of the transient near-infrared absorption was observed, indicating that no I_2^- was formed. In a separate series of experiments in colloid-free aqueous iodide solution at pH = 12 (0.1 M KI), transient I_2^- was readily detected upon irradiation with 266-nm Nd:YAG laser pulses (I^- ($h\nu$) $\rightarrow$ I + e^-(aq), I + I^- $\rightarrow$ I_2^-). The I_2^- was again monitored at 730 nm and found to decay according to a second-order rate law with a rate constant of 7×10^9 L mol^{-1} s^{-1}. This is in full agreement with the I_2^- disproportionation constant reported by Grossweiner.[21] Hence, if it were produced in the TiO_2 sol at pH = 12, I_2^- would be easily detected by the transient near-infrared absorption technique. Since none is observed, we conclude that I^- is not oxidized in aqueous TiO_2 colloid at pH = 12.

We have measured the I_2^- signal in the aqueous TiO_2 sol over a wide range of iodide concentrations, namely, from 10^{-4} to 10^{-1}

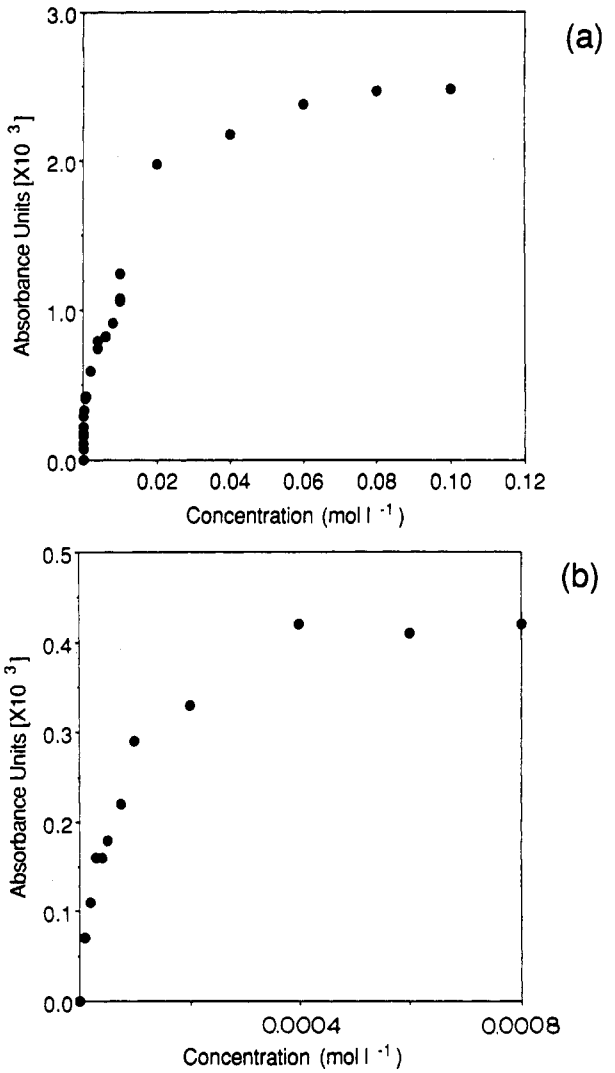

Figure 6. (a) Initial absorbance of the transient at 700 nm following 355-nm (2 mJ pulse $^{-1}$) excitation of aqueous TiO_2 colloid (6×10^{-7} M, pH = 2.7) plotted against concentration of KI. (b) Expanded plot of the concentration regime below 10^{-3} M I^-.

M. Plots of the I_2^- yield vs [I^-] (peak buildup) are displayed on two different concentration scales in Figure 6. Figure 6a shows that the I_2^- yield reaches a plateau near [I^-] = 0.1 M. Interestingly, the growth of the I_2^- yield with increasing iodide concentration is not smooth and reaches a first plateau at [I^-] = 10^{-3} M, as can be seen from the expanded plot in Figure 6b.

IV. Discussion

1. Rise of I_2^-. The fact that no oxidation of I^- occurs at all at negatively charged TiO_2 particles (pH = 12) supports the conclusion reached in earlier studies[6-8] that valence band holes are only scavenged by I^- species adsorbed on the semiconductor surface (I^-_{ads}). The driving force for this reaction is large at all pH values, namely, 1.6 V at pH = 2.7 and 1.0 V at pH = 12 ($E^0(I/I^-)$ = 1.33 V,[27] $E_{vb}(TiO_2, NHE)$ = 3.08–0.059 pH[6]). The transit time of a hole from the interior of the particle to the surface is on the order of picoseconds;[28] hence, formation of I_{ads} (reaction 3) is expected to be essentially complete within in the duration of the 5-ns laser excitation pulse at 355 nm. Reaction 4 represents the concurrent loss of free holes by recombination

$$h^+_{vb} + I^-_{abs} \rightarrow I_{ads} \quad (3)$$

$$h^+_{vb} + e^-_{cb} \rightarrow \Delta \quad (4)$$

with trapped conduction band electrons.[15] An alternative pathway leading to transient I atoms is possible in principle, namely, trapping of free valence band holes in the form of surface OH radicals,[29,30] O radical anions,[20,31] or peroxides,[32,33] followed by reaction of these species with I^-. However, formation of such surface species is too slow at pH = 3 (rise time $\approx$ 250 ns)[15] to explain the observed fast rise of I_2^- at [I^-] > 5×10^{-4} M (Figures 2 and 3). We conclude that it is unlikely that oxidation of I^- via surface trapped holes plays a significant role.

Surface-adsorbed I atoms formed by process 3 react with I^- to yield I_2^-. The plot of the observed pseudo-first-order rise constant against iodide concentration, Figure 3, points to the dominant participation of I^- from the surrounding solution (Eley–Rideal mechanism,[34] eq 5) rather than I^- adsorbed on the particle

$$I_{ads} + I^- \rightarrow I_2^- \quad (5)$$

surface. The reason is that k_{obs} depends linearly on the bulk I^- concentration not only in the 10^{-4}–10^{-3} M range as shown in Figure 3 but even up to [I^-] = 0.01 M (the 1/e rise observed for [I^-] = 0.01 M, Figure 2b, agrees with the rise time of 12 ns predicted by the slope of the plot in Figure 3). While such a linear dependency on [I^-] is expected in the case of the Eley–Rideal mechanism, k_{obs} would exhibit a curve-shaped dependency typical for a Langmuir adsorption isotherm if predominantly surface-adsorbed iodide ions were reacting with I_{ads}. Since the data do not indicate any deviation from linearity, we propose that I_2^- is mainly formed by reaction of surface-adsorbed I atoms with I^- from solution. It is interesting to note that while the reaction of I with I^- in homogeneous solution is diffusion controlled,[35] the bimolecular rise constant for reaction 5 of 7.9×10^9 L mol^{-1} s^{-1} is significantly lower than the diffusion-limited rate constant of 8×10^{10} L mol^{-1} s^{-1} calculated for TiO_2 particle–I^- encounters by the Smoluchowski formula[36]

$$k_{diff} = 4\pi d_{AB} D N_A \quad (6)$$

(d_{AB} = 55 Å, $D = 1.87 \times 10^{-5}$ cm^2 s^{-1} [37]). The lower value in the case of I atoms adsorbed on TiO_2 particles is most probably due to the fact that on average only one I atom is formed per particle (section III). Hence, the probability of an I^- encountering a TiO_2 particle with I_{ads} in the proper position for reaction to occur is not expected to be unity.

Our experimental results agree with those obtained in the earlier studies[6-8] where a comparison is possible, i.e., at iodide concentrations of 0.01 M and higher. The 10-ns rise time of I_2^- observed at [I^-] = 0.01 M (Figure 2b) is consistent with the previous reports that I_2^- rises within the UV laser pulse used for band-gap excitation (10-30 ns).[6-8] Similarly, for [I^-] $\geq$ 0.01 M, our I_2^- yield vs [I^-] plot (Figure 6a) has the shape of a Langmuir adsorption isotherm as obtained by the previous groups. While these data at high iodide concentrations (>0.01 M) clearly show that the photogenerated valence band holes are overwhelmingly scavenged by surface-adsorbed I^-, our data in the 10^{-4}–10^{-2} M concentration range presented here give for the first time insight into the detailed reaction pathway that leads to formation of I_2^- (eqs 3–5).

Aside from the rate-limiting reaction step (5), two processes play a role in the formation of I_2^-. One of them, recombination of trapped electrons and free holes (reaction 4), is operative even at high iodide concentration as the I_2^- yield per electron-hole pair remains well below one (16%) at [I^-] = 0.1 M. The departure of the I_2^- yield vs iodide concentration curve from a smooth increase around [I^-] = 10^{-3} M (Figure 6) points to a second process that interferes with I_2^- formation. A similar deviation was previously observed in the case of I^- photooxidation at dye (phenylfluorone) sensitized TiO_2 colloid[10] and attributed to electron recapture by transient I atoms

$$e^-_{cb} + I_{ads} \rightarrow I^-_{ads} \quad (7)$$

Occurrence of this process is not surprising in view of the estimated

1.6-V driving force at pH = 2.7. The electron recapture rate constant of reaction 7 is expected to be sensitive to the microenvironment of the transient I atom on the TiO_2 surface. Hence, a spread in microenvironments may explain the nonmonotonous I_2^- yield vs $[I^-]$ behavior as discussed in more detail in our previous report on the sensitized TiO_2/I^- system.[10]

An interesting finding is that in the case of the bare TiO_2 colloid, the bimolecular rise constant of I_2^- (8×10^9 L mol^{-1} s^{-1}) is over 50 times larger than for phenylfluorone (PF) sensitized TiO_2 particles (1.2×10^8 L mol^{-1} s^{-1}).[10] Although the solvents used in the two cases were not the same (water vs ethanol), we believe that this large difference in I_2^- growth kinetics is not merely a solvent effect. It originates most probably from different TiO_2 surface charges for sensitized and bare colloid. The strong positive charge of bare TiO_2 particles is partially removed upon loading of the surface with phenylfluorone since chelation of the dye results in deprotonation of the sensitizer.[11] The result is a smaller Coulombic attraction of I^- surrounding the PF-sensitized TiO_2 particle surface.

2. Decay of I_2^-. The large bimolecular rate constant for reaction 2 of $>10^{10}$ L mol^{-1} s^{-1} implies efficient interfacial electron transfer from TiO_2 to I_2^-. The rate constant k_{et} for interfacial electron transfer can be obtained from the measured bimolecular decay constant k by aid of the expression[28,38]

$$\frac{1}{k} = \frac{1}{4\pi r^2}\left(\frac{1}{k_{et}} + \frac{r}{D}\right) \tag{8}$$

(r, sum of the radii of the TiO_2 particle and I_2^-; D, sum of the diffusion coefficients of I_2^- and TiO_2 particle; k_{et}, in cm s^{-1}; k, in cm^3 molecule^{-1} s^{-1}). For $[I^-] = 0.02$ M and pH = 2.7, we determined k as 4.3×10^{-11} cm^3 molecule^{-1} s^{-1} (section III.2). With $r = 55$ Å and $D(I_2^-) = 2 \times 10^{-5}$ cm^2 s^{-1} [37] ($D(TiO_2)$ is negligible), one calculates from eq 8 k_{et} as 15 cm s^{-1}. This is a large interfacial transfer rate constant, yet it is still somewhat smaller than D/r. Hence, under these conditions, reaction 2 is strongly influenced by both interfacial electron transfer and the rate of diffusional encounters of I_2^- with TiO_2 particles.[28]

The high value of k_{et} can readily be understood in terms of the large overvoltage that drives this interfacial electron transfer. According to the Tafel equation, k_{et} depends on the overvoltage $E - E^\circ$ at $T = 298$ K as follows:[13]

$$k_{et} = k_{et}^\circ 10^{-(\alpha/0.059)(E-E^\circ)} \tag{9}$$

(k_{et}°, electron-transfer rate constant for zero overvoltage; α, transfer coefficient). We can approximate the overvoltage $E - E^\circ$ by $E_{cb}(TiO_2) - E^\circ(I_2^-/2I^-)$, i.e., by the difference between the potential of the conduction band and the standard potential of the $I_2^-/2I^-$ couple. $E^\circ(I_2^-/2I^-) = 1.03$ V,[39] and $E_{cb}(TiO_2) = -0.12 - 0.059$ pH[40] (all voltages vs NHE). At pH = 2.7, this gives a large driving force of 1.3 V for electron transfer from TiO_2 to I_2^-. As the pH dependence of $E_{cb}(TiO_2)$ shows, the potential of the conduction band becomes more negative as the pH increases. By contrast, $E(I_2^-/2I^-)$ is independent of pH. This readily explains the substantial (2/3) increase of k when raising the pH from 1 to 2. For $r = 55$ Å and $D = 2 \times 10^{-5}$ cm^2 s^{-1}, a 66% increase of k reflects about a 2-fold rise of k_{et} according to eq 8. This implies a transfer coefficient α of 0.3 according to expression 9. It is an entirely reasonable value[28] and further strengthens our interpretation of the decay of I_2^- in terms of reaction 2. Note, however, that eq 9 only takes into account the effect of the pH on the overvoltage. Brown and Darwent have established that k_{et} is also affected by the accompanying change in ionic strength.[41]

The slower decay of I_2^- in the case of the glycerol colloid compared to the aqueous sol reflects the much lower diffusion coefficient in this highly viscous solvent. The viscosity of H_2O at 20 °C is 10 cP,[42] compared to 1340 cP for glycerol/methanol = 10/1.[42] Since the diffusion coefficient is inversely related to the viscosity according to the Stokes–Einstein law,[43] the ratio D/r drops from 36 cm s^{-1} for H_2O to 0.03 cm s^{-1} for the glycerol/methanol mixture. Hence, in the latter case $D/r \ll k_{et}$, which means that the reaction is expected to be mass-transfer-limited, and the Smoluchowski formula (eq 6) is expected to hold.[28] With $r = 55$ Å and $D = 1.5 \times 10^{-8}$ cm^2 s^{-1}, the bimolecular rate constant would be 6×10^7 L mol^{-1} s^{-1}, consistent with the observed slow decay of I_2^-. Note that the very slow decay rules out the possibility that I_2^- is reduced by trapped electrons at the colloidal particle on which it was formed.

An intriguing finding is that the predominant I_2^- decay mechanism in the case of bare TiO_2 colloid is combination with trapped conduction band electrons, while for phenylfluorone-sensitized TiO_2 particles (in ethanol) I_2^- decayed exclusively by disproportionation to yield I_3^-.[10] We believe that this is principally due to the fact that chelation of phenylfluorone to the TiO_2 particle very efficiently removes surface states which otherwise would act as conduction band electron traps.[11] The result is that reducible species other than I_2^- that are present in the sol and whose overpotential for reduction by TiO_2 electrons is smaller than $E - E^\circ$ of I_2^- may compete for trapped electrons. A main candidate is O_2 ($E^\circ(O_2/HO_2) = -0.125$ V[44]). The reduction potentials of this species are substantially more negative than $E^\circ = +1.03$ V of the $I_2^-/2I^-$ couple.[39] Removal of conduction band electrons by O_2 would disfavor process 2 relative to disproportionation of I_2^- (reaction 1). This interpretation is supported by the observed strong decrease of the I_3^- yield when deaerating the phenylfluorone-sensitized TiO_2 colloids.[10]

V. Conclusions

The main result of this work is the observation of the rise of the one-electron oxidation intermediate I_2^- following band-gap excitation of bare TiO_2 colloidal particles in aqueous iodide solution. These measurements are made possible by a very sensitive transient absorption technique based on a cw dye laser double-beam system. The rise of I_2^- ($k = 7.9 \times 10^9$ L mol^{-1} s^{-1}) is attributed to the reaction of surface-adsorbed I atoms with iodide from the surrounding solution. I_{ads} is formed by the reaction of surface-adsorbed iodide with valence band holes within the 5-ns duration of the 355-nm band-gap excitation pulse. Our ability to resolve the rise of I_2^- opens up the possibility of directly monitoring the transient I atom that precedes the formation of I_2^-, work that is in progress in our laboratory.

The decay of I_2^- is dominated by the reaction with trapped conduction band electrons. Disproportionation to yield I_3^- accounts for only 4% of the I_2^- decay in this bare aqueous TiO_2 sol. Comparison with our previous study of iodide photooxidation at phenylfluorone-sensitized TiO_2 particles[10] suggests that quenching of I_2^- by trapped conduction band electrons can be suppressed by chelating a dye to the TiO_2 surface. This effectively removes surface states that otherwise would act as long-lived conduction band electron traps.[11] In the absence of the stabilizing traps, conduction band electrons have sufficient driving force for efficient removal by species like O_2 that are less easily reduced than I_2^-.

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