Photoproduction of I_2 , Br_2 , and CI_2 on n-Semiconducting Powder

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The halogen molecules, Cl₂, Br₂, and I₂, have been successfully photoproduced in oxygen-saturated aqueous solutions containing the respective halide ion and platinized semiconducting $n-TiO_2$ powder. While the latter is produced photocatalytically, the first two are clear examples of products of photosynthetic reactions. These photosynthetic reactions carried out on the Pt-TiO₂ powders can lead to a net conversion of solar energy to storable chemical energy. The platinized TiO₂ powders are considered to be many short-circuited platinumsemiconductor electrodes on which the photoassisted reactions take place (i.e., the reduction of oxygen on the platinum sites by the photoproduced electron and the oxidation of the halide ion by the photoproduced hole on the TiO_2 surface). Although the oxidation of iodide ions by oxygen is thermodynamically spontaneous at pH 5.5, the oxidation rate is significantly enhanced in the presence of the $Pt-TiO_2$ powder and UV radiation. The oxidation of bromide and chloride ions by oxygen is nonspontaneous at pH 5.5, but they are oxidized at significant rates in the presence of the $Pt-TiO_2$ powder and UV radiation, indicating a photosynthetic process for the production of these halogens. Experiments indicate that the oxidation of the halide ions by oxygen will take place in the presence of irradiated unplatinized TiO₂ powder, but the reaction rate is significantly increased by platinization of the semiconducting powder. These results suggest that platinization is effective in producing, at the TiO_2 -electrolyte interface, a depletion region which is important for the efficient charge separation of the photoproduced electron-hole pairs. The photooxidation of the halogens was carried out at several pH values and for various conditions, and conclusions concerning the efficiency of the overall process are discussed.

Introduction

In the past few years, there has been considerable effort to develop methods for converting sunlight into valuable chemicals for energy storage or other purposes using semiconductors immersed in electrolyte solutions.¹ Photoassisted catalysis and photoassisted synthesis of some chemicals have been demonstrated with semiconductor electrodes which are usually electrically biased.¹ In order for a photoassisted oxidation reaction to occur in solution on n-type semiconductor surfaces without external bias, the flat-band potential of the semiconductor must be at a more negative potential than the reduction process. Some work has been done using n-type semiconductor powders^{2,3} and platinized n-type semiconductor powders^{4,5} to photocatalyze oxidation reactions which otherwise would occur at very low rates. The platinized semiconductor powder can be considered to provide many short-circuited, platinum-semiconductor electrodes on which photoassisted reactions can take place, provided the reduction process occurs at a more positive potential than the flat-band potential of the semiconductor. To date, most of the reactions reported taking place at illuminated TiO_2 or Pt-TiO₂ powders are, by their nature, photocatalytic.^{2-7,12} A possibility of carrying out photosynthetic reactions is of greater interest.^{12,16} We report here the successful photosynthetic production of Br₂ and Cl₂ and the photocatalytic production of I₂ from aqueous solutions of their respective ions in the presence of the $Pt-TiO_2$ powder.

Experimental Section

The reaction cell consisted of 35-mL solutions of 2-3 M concentrations of KI, KBr, or NaCl and 100-200 mg of Pt-TiO₂ powder. The powder was prepared by irradiating a suspension of 2 g of lightly doped TiO₂ powder in mixture of chloroplatinic acid and acetic acid (1:1) pH 4 to get

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 Pt/TiO_2 1:10 by weight.⁶ The anatase powder was doped by heating to 650 °C under hydrogen for 8 h. Air or oxygen was passed through the cell, and the stirred solution was exposed to 1000-W high-pressure mercury lamp focused through a flat-glass window on the cell. The power measured at the cell window was $400 \text{ mW}/\text{cm}^2$ as determined with a thermopile detector.

Two methods were used to determine the halogen production rate. In one method, the solution was saturated with oxygen and the cell remained sealed with a positive oxygen pressure above the solution for the irradiation period. After irradiation, the amount of halogen produced was determined by using the standard iodometric titration

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Figure 1. Quantity of halogen produced as a function of illumination times obtained at different pH values.

method. The total amount of halogen produced was determined by adding the amount of halogen found in solution to the amount of halogen in the vapor phase (calculated by using known values for the equilibrium constant of $Cl_2(solution) \rightleftharpoons Cl_2(gas)^8$).

In some experiments, the cell was not closed during the irradiation period, but the oxygen was passed continuously through the cell and through three external traps arranged in series and containing ~ 35 mL of the same halide solutions as in the reaction cell or distilled water. After the irradiation periods, the quantity of halogen present in the reaction cell and in each of the traps was determined and summed.

In a second method, a known amount of As(III) was introduced initially into the halide solution. After illumination, the solution was titrated with I_2 in the presence of starch to determine the amount of As(III) remaining. The difference between the initial and final amounts of As(III) in solution was taken to be the quantity of halogen produced. In this method, oxygen was continuously bubbled through the solution during the period of illumination. Control experiments were also conducted.

Results and Discussion

Within 1–15 h of irradiation of the halide solutions containing the Pt-TiO₂ catalyst, the solutions became colored with the respective halogen colors (dark brown for the I⁻ solution, light yellow for the Br⁻ solution, and light yellow-green for the Cl⁻ solution). Simple I_2 /starch tests revealed that the solutions contained the halogen molecules. Smaller amounts of the halogens were produced under the same conditions when the cells contained a suspension of unplatinized TiO₂ powder. These experiments were repeated under different pH conditions and for different time periods. Some of the results are summarized in Table I and in Figure 1. Several points (to be discussed later) should be noted: (a) Halogens can be produced by irradiating solutions containing pure TiO₂ powder catalyst, but the production rates are greatly enhanced by using the platinized TiO_2 powders. (b) The rate

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TABLE I:	Comparison	of Halogen	Production
for Catalyst	s and pH	-	

solution	pH ^a	catalyst ^c	irradiation time, ^d h	amount produced, µmol
1.7 M KBr	7.0^{b}	100 mg Pt-TiO,	1	140 ^e
1.7 M NaCl	7.0^{b}	100 mg Pt-TiO,	1	98^e
2.0 M KI	5.5	none	2	1.4
2.0 M KI	5.5	$150 \text{ mg Al}_2 \text{O}_3$	2	2.3
2.0 M KI	5.5	150 mg TiO ₂	2	3,5
2.0 M KI	5.5	150 mg Pt-TiO_2	2	4.9
2.0 M KI	5.5	150 mg Pt-TiO ₂	4	10.8^{f}
2.0 M KI	2.0	150 mg Pt-TiO_2	2	158
3.0 M KBr	5.5	150 mg TiO ₂	40	1.3
3.0 M KBr	5.5	150 mg Pt-TiO ₂	3	0.9
3.0 M KBr	5.5	150 mg Pt-TiO_2	23	6.2
3.0 M KBr	1.8	150 mg Pt-TiO_2	3	11
3.0 M NaCl	5.5	$150 \text{ mg Pt-TiO}_{2}$	3 .	0.9
3.0 M NaCl	5.5	200 mg Pt-TiO_2	24	2.6
3.0 M NaCl	1.2	150 mg TiO ₂	40	4
3.0 M NaCl	1.2	150 mg Pt-TiO_2	3	13
3.0 M NaCl	1.2	150 mg Pt-TiO_2	20	40

^a Adjusted by adding H_2SO_4 or NaHCO₃. ^b Adjusted by adding NaHCO₃. ^c Pt-TiO₂ prepared according to ref 6 with doped TiO₂ anatase. TiO₂ powder was undoped anatase. ^d 1000-W high-pressure Hg lamp irradiated through pyrex window. ^e Determined by initially introducing a known amount of As(III) to the cell. The As(III) also reacted, but at a lower rate than that of the halide as determined by blank experiments. ^f Determined by continuously passing oxygen through the cell and through two external traps, each containing $35 \text{ mL of } 2 \text{ M KI solution, and titrating with As(III) both the I₂ in the irradiated cell and the I₂ trapped in the two external traps.$

of halogen production is in the order $I_2 > Br_2 > Cl_2$. (c) There is some nonlinearity in the amount of halogen produced as a function of irradiation time, especially for the case of Cl_2 . This saturation effect can be reduced by continuously sweeping the halogen from the solution. (d) The halogen production rates measured by the second method (i.e., where As(III) was initially introduced into the reaction cell) is higher than the production rate measured by the first method. (Compare the results given in the upper part of Table I to the results in the rest of the table.) (e) The production rate of the halogens is dependent on the solution pH. Lowering the pH enhances the production of the halogens.

The chemical reactions considered to lead to these results are expressed in eq 1-3. The half-reactions assumed are

$$2X^- + 2h^+ \rightarrow X_2 \tag{1}$$

at the illuminated TiO_2 site, and

$${}^{1}/{}_{2}O_{2} + 2H^{+} + 2e^{-} \rightarrow H_{2}O$$
 (2)

at the platinized site, giving the overall reaction:

$$2X^{-} + \frac{1}{2}O_{2} + 2H^{+} \rightarrow X_{2} + H_{2}O$$
(3)

The energetics of the processes described by eq 1-3 for the three halogens are shown in Figure 2. The oxidation levels of the halides and water, as well as the band edge of TiO₂, are shown in this figure at both pH 5.5 and pH 1.0. As can be seen, the oxidation of I⁻ to I₂ by oxygen is a spontaneous reaction. Adding the Pt-TiO₂ photocatalyst, however, enhances the oxidation rate, as shown in Table I. More striking is the photooxidation of Br⁻ and Cl⁻ at the Pt-TiO₂ powder surface. The oxidation of these halides by oxygen is nonspontaneous at pH 5.5 with ΔG = +8 kcal/mol for Br⁻ oxidation and ΔG = +21 kcal/mol for Cl⁻ oxidation.¹³



Figure 2. Oxidation levels of the halides, water, and the band edges of TiO₂ at pH 1 and 5.5.

However, they can be oxidized at the Pt–TiO₂ surface upon irradiation as indicated in Table I. These are clear examples of a chemical reaction taking place at the illuminated Pt-semiconductor powder surface in a nonspontaneous direction (photosynthesis), giving rise to the production of useful chemicals. The photosynthetic reduction of Cu²⁺ on TiO₂ powder has previously been reported.¹² However, saturation (steady state) of the Cu deposition was reached after a period of irradiation. This occurred when the deposited Cu metal was oxidized upon irradiation in preference to water oxidation. In the case of copper as opposed to the halogen system described here, there is no simple way to make the reaction irreversible and there is no net chemical reaction after a long period of irradiation.

In order for a reaction to occur in the photosynthetic direction at the illuminated platinized n-semiconductor powder, there must be an effective separation of the photoproduced electron-hole pair in the semiconductor. Otherwise, the oxidation of the halide by hole capture would immediately undergo reduction by electron capture with no net halogen production.

The fact that photosynthesis is clearly achieved in this system indicates that charge separation occurs in the semiconductor powder (without external biasing) by introducing the platinum. With pure powder, much smaller rates were found, indicating that charge separation was not effective (see Table I and Figure 1). The effect of platinization is associated with the fact that the overvoltage for oxygen reduction at the particle is lowered.^{7,9}

The fact that the rates of production of the halogens are in the order $I_2 > Br_2 > Cl_2$ is due to the difference in the ability of the halide anions to compete with water for the photoproduced holes in the semiconductor^{1e,10,11} and also due to the difference in the ability of oxygen to compete with the halogen for reduction on the platinum site. Chlorine will compete with oxygen better than the Br_2 and I_2 , giving rise to higher recombination rates. The latter may be the cause for the nonlinear behavior (amount of halogen produced as a function of time) observed for long irradiation times since the halogen is allowed to accumulate

The Journal of Physical Chemistry, Vol. 85, No. 15, 1981 2257

in the solution (see Table I and Figure 1). This may be especially true for the case of chlorine. The important advantage of the system described here is the fact that this saturation effect may be reduced (or even eliminated in the ideal case) by sweeping the halogen molecules from the solution and thus making the process irreversible. This was demonstrated in some experiments when some of the halogen molecules were swept out of the reaction cell during the irradiation period to external traps. In this case, the halogen was not allowed to accumulate in the cell, making the overall process less reversible and more efficient. Higher rates of halogen production can be achieved by more efficient removal of the halogen from the reaction cell. The results shown at the upper part of Table I, in fact, represent the ideal cases where the halogen produced in the solution is instantly removed chemically through oxidation of the As(III) present in solution. In this case, high rates and high-quantum efficiencies are obtained. Of course, this is not a practical case, but one could approach this ideal case by efficiently removing the volatile halogens from the reaction cell during illumination. It is especially important in the system described here where a photosynthetic reaction is carried out (production of Br_2 and Cl_2) as compared to a photocatalytic reaction. In the first case, the photoproduced chemicals Br_2 and Cl_2 , if allowed to remain in solution, will tend to be reduced in preference to the reduction of the other reducible chemicals (O_2 in our case), so they must be removed from the solution.

The fact that the rate of the halogen production is enhanced by lowering the pH of the solution (see Table I) is understood from eq 1–3 and Figure 2. Two reasons may be given to explain this: (a) The oxidation potential of water is more positive at lower pH; therefore, halide oxidation becomes more competitive. (b) The reduction potential of oxygen is more positive at lower pH; therefore, oxygen becomes more competitive with the halogen molecules for reduction at the platinum sites. In fact, at the lower pH, the oxidation of Br⁻ becomes photocatalytic, as can be seen from Figure 2.

Quantum and Energy Efficiency

The experimental quantum efficiency (i.e., electrons per absorbed photon) for the Br₂ production in the presence of platinized TiO_2 powders for the ideal case where every Br_2 produced is instantly removed by the As(III) present in solution is $\sim 30\%$. It was assumed that $\sim 25\%$ of the measured 400 mW/cm² white light was the power capable of being absorbed by the anatase TiO_2 . (Ca. 25% of the power from high-pressure mercury lamps corresponds to photon energies greater than the band gap of TiO_2 , 3 eV). Taking into consideration that water is also being oxidized in competition with the halide oxidation,^{1e,10,11} the total quantum efficiency (electrons/photons) at the $Pt-TiO_2$ powder is expected to be higher than 30%, ^{1e,10,11} and, taking into account the ~ 0.5 current efficiency for Br⁻ oxidation given in ref 1e, 10, and 11 it is estimated to be $\sim 60\%$. These quantum efficiencies are similar to the values obtained with crystalline TiO₂ electrodes.^{1e,14} They indicate that the cathodic half-reaction taking place on the Pt sites is capable of polarizing the semiconducting particles to a very positive bias where the photocurrent at the semiconducting site reaches its saturation value.

For the photoproduction of Cl_2 in the ideal case (upper part of Table I), the quantum efficiency of ~20% is obtained. The ratio of the quantum efficiencies for the photoproduction of Cl_2 and Br_2 is 0.7, which is very similar to the value reported^{1e,10,11} for the photoproduction of the same chemicals where an external voltage is applied. It reflects the difference in the ability of Br^- and Cl^- to

compete with water oxidation at the semiconductor. In the less ideal case where the halogen molecules are allowed to accumulate in the solution, the quantum efficiencies for the halogen production are much lower and they depend on pH as discussed before. Thus, for basic pH, quantum efficiencies of 0.6%, 0.07%, and 0.07% are calculated for I_2 , Br_2 , and Cl_2 , respectively (from Table I), and 19%, 0.9%, and 1%, respectively, for the production of the halogens in the more acidic solution. For longer irradiation times, the quantum efficiencies drop even more as the halogen concentration in the reaction cell increases. However, as we observed, the efficiency could be increased when the halogen is swept out of the reaction cell. The estimated values for the quantum efficiency for Br₂ production would be 1-30% depending on the efficiency of the removal of the halogen from the reaction cell.

In the case of the photosynthetic reactions demonstrated above, net conversion of solar energy to chemical energy is also achieved. The efficiency for this conversion can be calculated by using the equation

$$\eta = \{ [energy stored as X_2] -$$

[energy from power supply]}/[energy from light] (4)

$$\eta = i[V_{\text{prod}} - V_{\text{suppl}}]t/[\text{light energy}]$$

where t is the illumination time, i is the rate of X_2 production expressed in units of current, V_{prod} is the difference in the redox potentials of the two half-reactions of the cell, and V_{suppl} is the voltage supplied from an external source. In our case, the photosynthetic reaction is carried out without supplying electrical power from an external source; thus $V_{\text{suppl}} = 0$. Taking into consideration only the light absorbed by the TiO₂, the calculated optical power efficiency for the ideal case of Cl₂ production is 3% (this is compared to the 1–2% solar-to-electrical energy-conversion efficiency at TiO₂ electrodes¹⁴). In the acidic solution, where Cl₂ is allowed to accumulate, a power efficiency of 0.03% is calculated for the conversion of solar-to-chemical energy. The practical values for the efficiency would be somewhere between these values. If the whole spectrum of available light energy is taken into consideration, the efficiencies calculated are lower.

Conclusions

Photoproduction of the halogens I₂, Br₂, and Cl₂ from the respective halide solutions at the $Pt-TiO_2$ catalyst was demonstrated. The latter two products are a result of a photosynthetic route giving rise to a net conversion of radiant energy to chemical energy. The quantum efficiency for the process increases with decreasing solution pH. The reverse reaction can be slowed (or eliminated) by removal of the halogen from the reaction cell. in the ideal case where no back-reaction is allowed by fast removal of the halogen, the quantum efficiency for halogen production can reach 30% with illuminated $Pt-TiO_2$ electrodes. For the case of chlorine production, the solar-to-chemical energy-conversion efficiency would be between 0.03% and 3% (when O_2 is used as the oxidizing agent) depending on the rate of halogen removal from the reaction vessel. The photoproduction of the halogens at Pt-TiO₂ particles may be of a practical value if the halogen is efficiently removed from the reaction cell.

Oxidation of NO₃⁻ and Cl⁻ by the Primary Solvent Cation. A Pulse Radiolysis Study

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The production of NO₃ and Cl_2^- radicals in the pulse radiolysis of NO₃⁻ or Cl⁻ solutions in water and acetone and the lack of this production in solutions in methanol, dioxane, and ammonia have been attributed to the oxidation of the solute anion by the primary solvent cation. This reaction proceeds in competition with proton transfer between the cation and the solvent molecule. Formation of NO₃ by the direct effect and of Cl_2^- by radical oxidation was found to be unlikely.

Introduction

Whereas a great deal of work has been devoted to studies on reactions of solvated and unsolvated electrons with molecules of various solvents only a few authors claim to have observed reactions of the corresponding primary solvent cations. In the scheme

$$BH \rightarrow BH^+ + e^- \tag{1}$$

$$BH^+ + BH \rightarrow BH_2^+ + B \tag{2}$$

 $BH^+ + S^- \rightarrow BH + S \tag{3}$

$$\mathbf{B} + \mathbf{S}^{-} \to \mathbf{B}^{-} + \mathbf{S} \tag{4}$$

where BH is the solvent molecule, B is the solvent radical, and S^- and S are the solute anion and radical, respectively, (1), (2), and (4) represent the well-known reactions of primary ionization, production of the solvent radical at the cost of the cation and oxidation of the solute anion by the solvent radical. All three reactions have been substantiated by vast experimental evidence, which is not the case for (3), the direct oxidation of the solute anion by the solvent cation without the intermediate step (2).

Actually, the demonstration of the validity of (3) involves considerable difficulties. The mass-spectrometry data prove (2) to be very fast which, in the liquid phase, usually makes (3) negligible, even in concentrated solutions. Moreover, even assuming that a significant fraction of BH⁺ may escape (2), it still remains to be proved that S is produced indeed in (3) and not in (4). As a consequence, reaction 3 has been hitherto discussed in respect to a few aqueous, methanolic, and acetonic solutions only.

In aqueous solutions oxidation of Cl^- by OH to Cl_2^- has not been unequivocally accepted, whereas it was proved that NO_3 is produced in the radiolysis of concentrated