THE JOURNAL OF
PHYSICAL CHEMISTRY

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J. Phys. Chem., **1986**, 90 (12), 2729-2732 • DOI: 10.1021/j100403a034

The Journal of Physical Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Photoinduced Oxidation of Bromide to Bromine on Irradiated Platinized TiO_2 Powders and Platinized TiO_2 Particles Supported in Nafion Films

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(Received: November 25, 1985)

The photoelectrochemical oxidation of bromide ion in oxygen-saturated solutions at irradiated TiO_2 powders and TiO_2 incorporated in Nafion films, in the presence and absence of Pt, was studied. As(III), added as a bromine scavenger in studies of bromine formation on TiO_2, can be oxidized directly at the Pt/TiO_2 surface so that previous estimates of the rates of Br_2 formation in these systems are probably too high. Spectroscopic evidence is presented for the formation of K_2PtBr_6 when platinized TiO_2 powder or platinized TiO_2-loaded Nafion films interact with oxygenated aqueous KBr in either light or dark. Formation of bromine by photoelectrochemical bromide oxidation occurs efficiently only after the platinum has been converted completely to $PtBr_6^{2-}$. The rate of Br_2 formation (per gram of photosensitive catalyst) is greater on TiO_2/Nafion films than on TiO_2 powders. The dependence of the rate on pH, amount of TiO_2, and irradiation time is reported.

Introduction

Previous reports from this laboratory have concerned the development of integrated chemical systems (e.g., CdS on supports like the perfluorosulfonate cation exchange polymer, Nafion, and silica with various catalysts)[1] for photochemical reactions. The work described here concerns the photooxidation of Br^- (in the presence of O_2) using TiO_2 powder and TiO_2 in Nafion.[2] Photochemical oxidation of halide ions to the corresponding halogens in competition with water oxidation has been reported using ZnO,[3] TiO_2,[4-9] RuO_2,[10] WO_3,[11] and platinized TiO_2[12] as photosensitizers.

Two experimental procedures are common. First, to measure the efficiency of the primary photoreaction, a chemical trap is added to assure the absence of back reaction of dihalogen. Second, to optimize the rate of the accompanying reduction reaction, small islands of metals having low overpotentials for hydrogen generation or oxygen reduction are deposited on the semiconductor. With either experimental modification, the overall chemical inertness of the trap and the deposited metal is assumed. With organic traps in nonaqueous suspensions, this assumption is clearly not justified and oxidation products obtained via chain reactions of the organic substrate are easily detected.[8b]

In this paper we demonstrate the production of Br_2 on Nafion/TiO_2; however, the efficiency is less than that projected from earlier studies of TiO_2 particulate systems. In reinvestigating such systems we found that caution must be exercised in interpreting rates of halide oxidation on irradiated semiconductor surfaces, because in aqueous suspensions, inorganic traps for dihalogen can be directly involved in primary photoelectrochemical processes and the noble metal catalysts deposited on the semiconductor can be chemically removed in the presence of bromide and/or bromine. Thus, we show that the high quantum efficiency for photoelectrochemical oxidation on Pt–TiO_2 (in the presence of As(III) which acts as Br_2 scavenger) previously attributed to Br^-/Br_2 interconversion[12] is, in large part, the result of direct oxidation of As(III) adsorbed on the surface of the Pt–TiO_2. Furthermore, we report spectroscopic evidence for the formation of K_2PtBr_6 from platinized TiO_2 powders or platinized TiO_2-loaded Nafion films suspended in oxygenated aqueous KBr solution. Thus, the low rate of bromine formation observed on Pt/TiO_2 is explained on the basis of a redox reaction involving oxidation of Pt via photogenerated Br_2. Finally, we report the results of a comparative rate study of bromide oxidation on irradiated TiO_2 (no Pt) as a powdered suspension and as dispersed particulates in Nafion films.

Experimental Section

All chemicals were analytical grade materials. The catalyst TiO_2 (MCB >99% anatase) was used as received. Platinization of anatase TiO_2 powder was achieved by photolysis of a suspension of the powder in aqueous H_2PtCl_6.[13] The platinum complex K_2PtBr_6 was prepared by a literature method.[14] TiO_2 was incorported into a Nafion 117 (equivalent weight 1100) membrane by following the previously described procedure.[2] The Nafion film was first boiled in concentrated HNO_3 and then in distilled water. the film was then soaked in an argon-saturated 0.1 M $TiCl_3$/methanol solution for 24 h. The purple film obtained was soaked in 3% H_2O_2 for 4 h after which the color had changed to orange. The film became colorless (transparent) after it was heated at 100 °C in an oven for 12 h. Prior to use, the film was boiled in distilled water. The X-ray diffraction spectrum of TiO_2-loaded films, prepared by the above method, showed peaks corresponding to anatase TiO_2.[15]

The degree of TiO_2 incorporation was controlled by varying the soaking time in $TiCl_3$/methanol solution. The amount of TiO_2 in the Nafion film was determined by boiling the film in 6 N H_2SO_4 until all of the incorporated TiO_2 was completely dissolved. Complete removal of titanium could be verified by immersing the film into H_2O_2 solution. (If TiO_2 remains within the film, an intense yellow color develops.) Acid washings were continued until all titanium was removed. The combined acid mixture was then neutralized and 5 mL of 3% H_2O_2 was added. The intensity of the yellow color of the resulting peroxytitanate was measured by absorption spectrophotometry from which the amount of supported titanium could be calculated from a calibration curve. The TiO_2 loadings in Nafion films are listed in Table III. Platinization of the TiO_2-loaded Nafion films was achieved by metal sputtering (600–1000 Å of Pt was usually deposited).

All irradiations were carried out in Pyrex vials under a positive oxygen pressure. For sample preparation, the appropriate amount of KBr solution (10–12 mL), containing 0–10^{-2} M H_3AsO_3, and

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TABLE I: Photoelectrochemical Production of Bromine and Consumption of As(III) on Platinized TiO_2 Powders[a]

	KBr concn, mM	H_3AsO_3 concn, mM	pH[b]	Pt/TiO_2, mg	irradn[c] time, h	μmol of Br_2[d] produced/h	μmol of As(III)[e] consumed/h
1	2.5	9.1	1.4	43.5	0.0[f]	0.00	0.55[f]
2	0.0	9.1	1.3	44.0	0.0[f]	0.00	1.6[f]
3	2.5	9.1	1.3	39.0	4.0	0.04	1.9
4	0.0	9.1	1.2	41.5	4.0	0.00	22.5
5	2.5	9.1	1.3	42.0	5.8	0.04	1.5
6	2.5	9.1	1.4	42.0	7.5	0.04	1.4
7	0.0	9.1	1.3	44.0	7.5	0.00	12.5
8	2.5	9.1	1.4	44.5	10.0	0.04	1.4
9	0.0	9.1	1.3	41.5	10.0	0.00	9.0
10	2.5	8.0	1.7	47.5	20.0	0.04	1.0
11	0.0	8.0	1.8	50.5	20.0	0.00	3.0
12	2.5	0.0	1.5	42.3	116.0	0.04	0.0
13	2.5	4.1	6.5	44.0	16.0	0.00	2.3
14	2.5	0.0	4.9	44.0	24.0	0.05	0.0
15	1.7	0.0	7.1	41.5	21.0	0.00	0.0
16	1.7	8.6	7.0	46.0	2.5	0.00	7.4
17	0.0	8.6	7.1	42.0	2.5	0.00	12.2

[a] The aqueous solutions were saturated with oxygen before photolysis. [b] pH was adjusted by using $NaHCO_3$ or H_2SO_4. [c] A 450-W high-pressure Xe lamp was employed (output power of 0.06 W/cm^2 at the cell's window; $\lambda_{excit} > 320$ nm). [d] Standard iodometric method was used for Br_2 determination; values are within ±10% error. [e] Corrected for dark reaction of As(III) (except for first two entries). [f] Dark reaction values after 13 h.

a weighed quantity of TiO_2 powder, Pt/TiO_2 powder, Pt/TiO_2/Nafion, or TiO_2/Nafion were introduced into a vial. The pH was adjusted by adding H_2SO_4, HCl, $NaHCO_3$, or NaOH. For samples with powdered photocatalysts, a small magnetic stirring bar was also placed in the vial for agitation of the mixture during the course of the irradiation. Samples were then stoppered with a rubber septum secured with a copper wire. Solutions containing powdered catalysts were sonicated for 20–30 min prior to oxygen purging (20–30 min). The irradiation was carried out using a focused 450-W high-pressure Xe lamp equipped with a water jacket and a Pyrex focusing lens to exclude excitation wavelengths shorter than 320 nm. The intensity at the cell's window was ~0.06 W/cm^2 (Coherent 210 power meter).

The adsorption of As(III) on Pt/TiO_2 was established via colorimetric determination of arsenic[16] as follows: a typical mixture for irradiation (Pt/TiO_2 and KBr/H_3AsO_3 solution) was stirred for several hours in the dark. After filtration, the solid was washed with hot water several times. A few drops of cold saturated Na_2MoO_4 solution was added to the powder followed by an excess of $SnCl_2$ in aqueous HCl. A blue color developed and did not disappear upon heating. This is a positive test for the presence of As(III) on the Pt/TiO_2 powder. Pt/TiO_2 samples that had not been exposed to As(III) gave no blue color when treated in the same way.

Two methods were employed for determination of Br_2 after irradiation. (A) Iodometric titration: a known quantity of As(III), as H_3AsO_3, was introduced into the bromine-containing sample. The mixture was titrated with a standard solution of I_3^- using a starch indicator. (B) Spectroscopic method: a Hewlett-Packard 8450A UV–vis spectrophotometer was employed to obtain the absorption spectrum of Br_3^- and K_2PtBr_6 formed in the photolysis mixture. (Br_2 exists as Br_3^- in the presence of large excess bromide ion, $Br^- + Br_2 \rightarrow Br_3^-$ where $K = 16.9$.)[17] A comparison of the intensity of the characteristic absorption band at 266 nm ($\epsilon = 46\,534$ M^{-1} cm^{-1}) for Br_3^- and 313 and 365 nm ($\epsilon = 16\,258$ and 6594 M^{-1} cm^{-1}, respectively) for K_2PtBr_6 with a calibration curve allowed calculation of the amount of bromine and K_2PtBr_6 complex in the photolyzed solution. The values determined by each method (for Br_2 formation) agreed to within experimental error.

Results and Discussion

Reaction at Pt/TiO₂ Particles. Near-UV irradiation of n-TiO_2 particles loaded with Pt in the presence of oxygenated aqueous KBr containing As(III) are summarized in Table I.

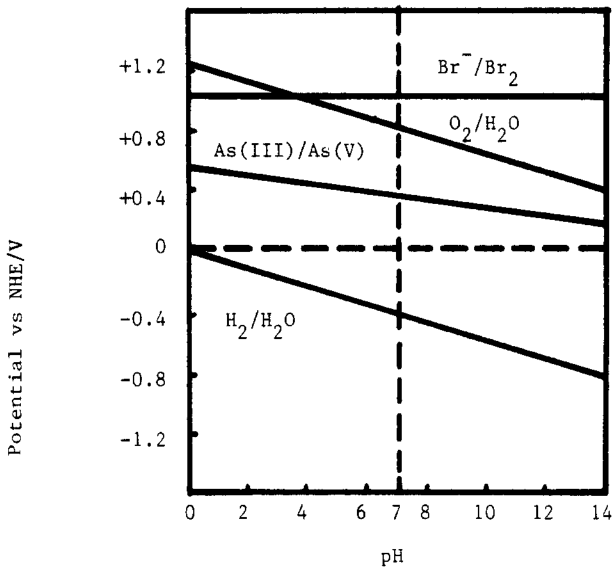

Figure 1. Oxidation potentials of bromide, arsenous, and water couples as a function of pH.

The following are evident from the data: (1) in the absence of KBr, As(III) is rapidly consumed in oxygenated solution in the dark and upon illumination (entries 2 and 4 in Table I), with light greatly accelerating the reaction; (2) the disappearance of As(III) in the presence of KBr is also fast (entries 1 and 3) and appears to be the dominant process.

The standard potential for the bromine/bromide couple, 1.05 V vs. NHE, is more positive than that for the oxidation of As(III), 0.35 V (adjusted to pH 7). If the rate of bromide and As(III) oxidation by the photogenerated holes were governed by overlap theory as predicted by Gerischer[18] then the bromide/bromine oxidation would have been expected to be more facile than As(III) oxidation (Figure 1). However, all previous experiments[4,5] have shown that the more negative $\Delta G°$, the faster (easier) the reaction. Moreover recent experiments by Gomes et al.[9] suggest a multistep mechanism for the oxidation of bromide, being assumed to occur with the surface intermediate H_2O_2 and ·OH formed by photoanodic oxidation of water. Thus, Br_2 and O_2 formation occurs via common reaction intermediates (H_2O_2 and ·OH), so that competitive kinetics governs the relative efficiency of Br_2 production.

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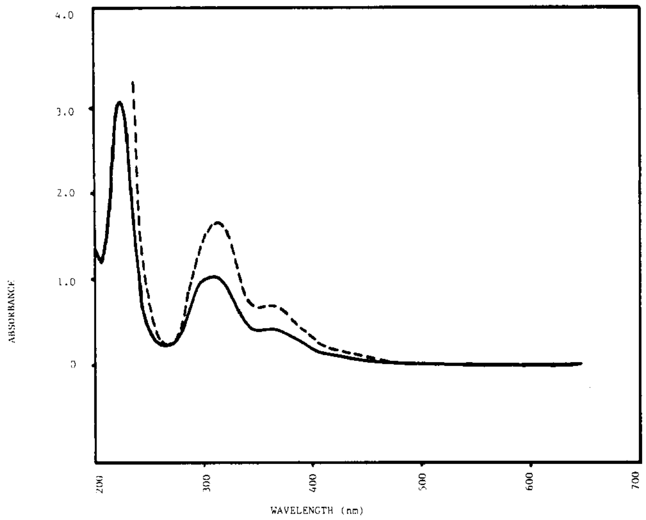

Figure 2. UV-vis absorption spectra of aqueous 1.33×10^{-4} M K_2PtBr_6 (dashed curve) and solution prepared by irradiating Pt/TiO_2 powder (or Pt/TiO_2-Nafion) in 3 M KBr (solid curve).

TABLE II: Dependence of K_2PtBr_6 Formation on pH[a]

	pH[b]	Pt/TiO_2, mg	μmol of K_2PtBr_6 produced[c]
1	0.6	41	2.0
2	1.1	41	1.9
3	2.5	41	0.7
4	3.3	41	0.4
5	4.6	41	0.1
6	7.0	41	0.09
7	10.5	41	0.08
8	2.6	6[d]	1.7

[a] [KBr] = 1.7 M throughout; the aqueous solutions were saturated with oxygen and allowed to stand in dark for 23 h with constant stirring; for each entry an identical sample was irradiated ($\lambda_{excit} > 320$ nm) in parallel for the same period of time and gave values to ±10% for the amount of K_2PtBr_6 formed thus suggesting no enhancement by light. [b] pH was adjusted by using HCl or $NaHCO_3$. [c] Determined spectroscopically. [d] Platinum black was employed.

Preferential adsorption of As(III) to the surface of $Pt-TiO_2$ may also be a factor in its oxidation at TiO_2. Although the results of our colorimetric analysis unequivocally showed that As(III) adsorbed, no attempt was made to obtain either quantitative adsorption data or an analysis of the surface. The rate of photoinduced As(III) oxidation (corrected for dark reaction) is suppressed in the presence of bromide (compare entries 3 and 4, Table I). This may be caused by the competitive adsorption of Br^-.

Since no bromine was detected at pH 7 in the absence of As(III) (entries 16 and 17 in Table I) and since As(III) is rapidly consumed by direct photochemical oxidation (entry 4 in Table I) we suggest that previous reports of high quantum efficiency for bromide (0.30) and chloride (0.20) oxidation on irradiated Pt/TiO_2 in the presence of As(III)[12] may have been complicated by direct, rapid photoelectrochemical consumption of As(III) rather than its mediated oxidation by Br_2. Our results indicate that when bromide is directly oxidized on TiO_2 (no As(III)) the overall oxidation efficiency is very low compared to the earlier work on Pt/TiO_2.[12] However, we did not evaluate, and thus cannot compare, efficiency losses inherent in the photoinduced electron exchange at the semiconductor-electrolyte interface and losses due to reductive back reaction of bromine.

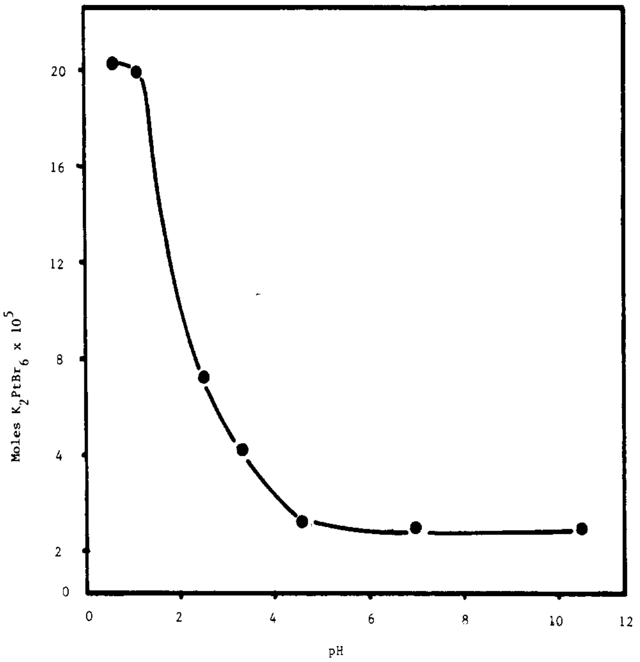

Figure 3. pH dependence of K_2PtBr_6 formation in aqueous KBr (1.7 M) containing Pt/TiO_2 powder. Reaction time was 23 h in the dark. Similar rates were observed with irradiation.

TABLE III: Photoelectrochemical Production of Bromine on Irradiated TiO_2/Nafion Films and TiO_2 Powders[a]

	catalyst[b]/ support, mg	pH[c]	irradn time,[d] h	mol of Br_2[e] produced $\times 10^7$	mol of $Br_2/(h \cdot mg)$[f] $\times 10^8$
1	1.86/Nafion	1.5	22	6.3	1.54
2	1.86/Nafion	2.5	22	5.4	1.32
3	3.70/Nafion	5.5	22	7.2	0.90
4	2.20/Nafion	7.0	22	3.8	0.80
5	1.86/Nafion	5.5	2.0	1.13	3.04
6	3.00/Nafion	5.5	2.0	2.0	3.33
7	4.10/Nafion	5.5	2.0	2.85	3.47
8	3.00/Nafion	5.5	4.8	2.4	1.67
9	3.00/Nafion	5.5	10	4.9	1.63
10	3.00/Nafion	5.5	14	4.8	1.14
11	3.00/Nafion	5.5	20	6.4	1.07
12	4.00/powder[g]	5.5	22	0.35	0.04
13	10.00/powder[g]	5.5	14	1.45	0.010
14	10.00/powder[g]	1.5	17	11.0	0.65

[a] [KBr] = 3.0 M; total volume of the sample was 10 mL throughout. [b] A 1.5 cm × 2.5 cm TiO_2/Nafion film was employed unless otherwise specified. [c] pH was adjusted by using H_2SO_4 or NaOH. [d] Light source was a 450-W high-pressure Xe lamp (power output at the cell's window = 0.06 W/cm^2; excitation wavelength $\lambda > 320$ nm). [e] Determined from the absorption spectrum of irradiated mixture. [f] Rate of bromine generation per hour and milligram of TiO_2. [g] Powdered TiO_2 (anatase) was used.

When $Pt-TiO_2$/Nafion films suspended in KBr solution were irradiated, the Pt layer slowly disappeared and the absorption spectrum of the irradiated mixture did not correspond to that of Br_3^- (which shows a characteristic absorption band at 266 nm). Rather, a red-shifted three-band (at 228, 313, and 365 nm, respectively) spectrum identical with that of an authentic sample of K_2PtBr_6, Figure 2, was obtained. Identical spectra were obtained when platinized TiO_2 powders were used. For the Pt/TiO_2 powder system, K_2PtBr_6 formed in the dark but at a slightly lower rate than when illuminated. The pH dependence of K_2PtBr_6 formation is summarized in Table II. The amount of K_2PtBr_6 formed in 23 h (dark or light) dropped as the pH increased (Figure 3). Since K_2PtBr_6 formation depletes bromine, the rate of Br_2 generation (1.0×10^{-3} mol/(h·mg)) reported in entry 12 of Table I does not reflect the true value of this rate. The observed rate is considerably lower than that seen on unplatinized TiO_2 (Table III).

Reaction at TiO_2/Nafion Systems. The rate of Br_2 formation was also studied as a function of pH, irradiation time, and the amount of catalyst (no Pt), using TiO_2 powder and TiO_2/Nafion films (Table III). As the pH drops the rate of Br_2 formation increases (Figure 4). A plausible explanation is that the increased efficiency of oxygen and proton reduction at low pH allows these species to compete more effectively with Br_2 for photogenerated

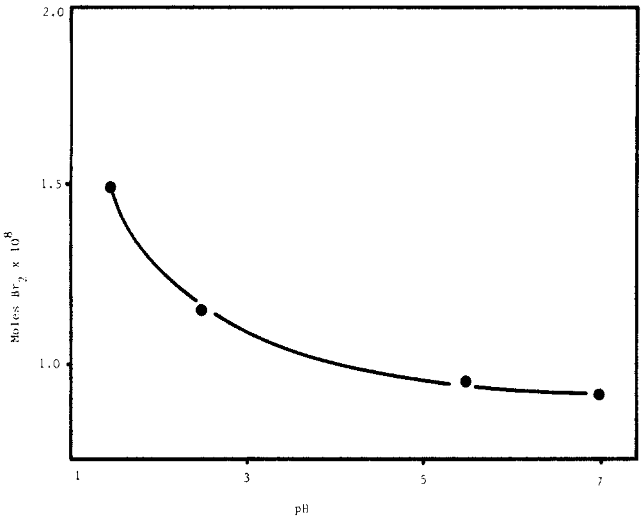

Figure 4. Amount of bromine generated on TiO_2 powders (no Pt) as a function of pH at constant KBr concentration (22-h irradiation).

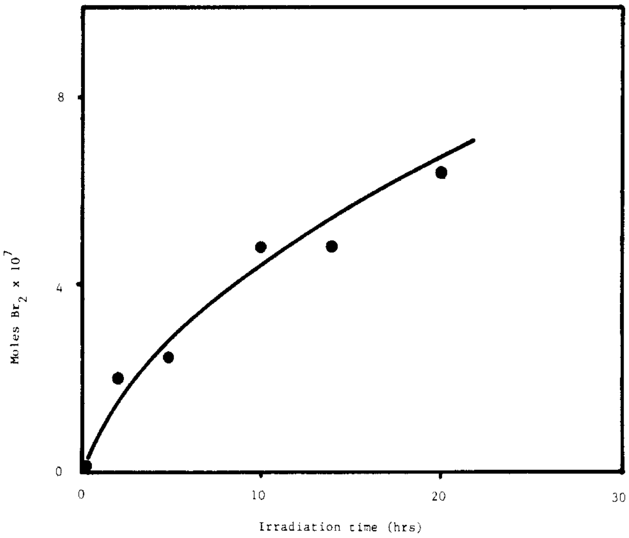

Figure 5. Photoelectrochemical production of bromine on irradiated TiO_2 powder at constant [KBr] = 3 M.

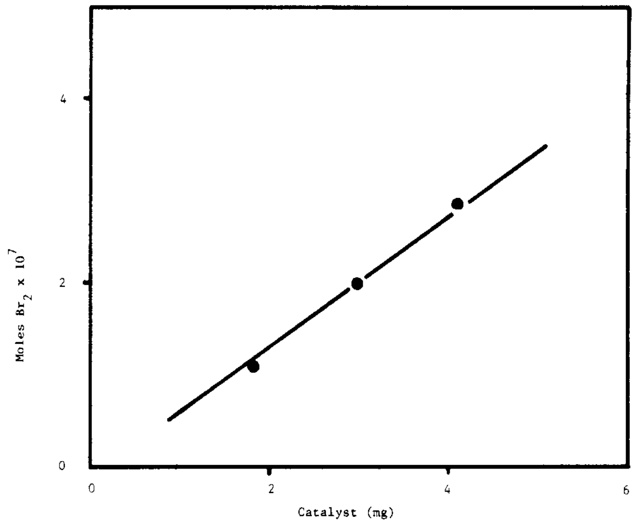

Figure 6. Production of bromine on irradiated TiO_2/Nafion films as a function of catalyst weight at constant pH and [KBr] = 3 M (2-h irradiation).

electrons. The production of Br_2 continues as the irradiation proceeds, although the rate begins to decrease at long irradiation periods, presumably because [Br_2] is reduced (Figure 5). As expected, an increase in the amount of TiO_2 irradiated is accompanied by an increase in Br_2 yield. Since the irradiated TiO_2 surface area in the Nafion films is approximately proportional to the amount of TiO_2 incorporated into the films, the linear relationship between Br_2 produced and TiO_2 weight (Figure 6) is understandable. The rate of bromine formation (per gram of semiconductor) is considerably lower on TiO_2 powders than on TiO_2/Nafion films (entries 7 and 12, Table III). Possible reasons are (a) a greater surface area may be exposed when TiO_2 is supported in Nafion and (b) interfacial electron transfer competes less effectively with electron–hole recombination.

Alternatively, a higher oxygen concentration in the perfluorinated Nafion membrane may promote the concomitant bromide reduction in the film compared with the suspended powder. Although the solubility of oxygen in Nafion films suspended in aqueous KBr was not measured, perfluorinated solvents commonly display much greater oxygen solubilities than aqueous solutions. In any case, Nafion is an excellent support for the dispersion of small photoactive particles,[19] and like our previous reports on CdS–Pt/Nafion films,[20,21] TiO_2 retains excellent photoelectrochemical activity when included within this ion exchange membrane.

Summary

In summary, we have demonstrated the following:

(1) Arsenic(III) adsorbed on the surface of platinized TiO_2 is oxidized more efficiently than dissolved bromide. Thus, its utility as a halogen scavenger should be viewed with caution, since this direct oxidation in addition to scavenging dihalogens leads one to overestimate the yield of photogenerated dihalogen.

(2) Oxidation of bromide to bromine on the surface of Pt–TiO_2, either in powdered form or in a Nafion film, is followed by reaction of bromine with Pt, leading to formation of $PtBr_6^{2-}$. To our knowledge this is the first report of the removal of Pt from TiO_2 during photoelectrochemical halide oxidation.

(3) The rate of bromine formation (per gram of semiconductor) is considerably greater on Nafion-supported TiO_2 than on TiO_2 powder, although it has not been unequivocally established whether this effect can be attributed to differences in particle size, defects, semiconductor-supported interactions, locally high O_2 concentration, or other factors.

Acknowledgment. This work was supported by the Gas Research Institute.

Registry No. TiO_2, 13463-67-7; Br^-, 24959-67-9; Br_2, 7726-95-6; As, 7440-38-2; Pt, 7440-06-4; K_2PtBr_6, 16920-93-7; KBr, 7758-02-3; Nafion 117, 66796-30-3.

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