J. Am. Chem. Soc. 1984, 106, 6565–6569

Visible Light Induced Oxygen Evolution in Aqueous CdS Suspensions

Nada M. Dimitrijević,[1] Shuben Li,[2] and Michael Grätzel*

Contribution from the Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne, Switzerland. *Received May 7, 1984*

Abstract: Aqueous dispersions of CdS loaded with noble metal oxides evolve oxygen under illumination with visible light in the presence of $PtCl_6^{2-}$ as scanvenger for conduction band electrons. The catalytic activity of Rh_2O_3 is superior to that of RuO_2 in promoting water oxidation under alkaline conditions. No oxygen is generated in the absence of redox catalyst.

Low band gap semiconductors in contact with aqueous electrolyte are subject to photocorrosion,[3] and this presents a serious problem for their application in solar energy conversion devices. Numerous attempts have therefore been made in the past to stabilize these materials. If an n-type semiconductor is to be employed in a device that decomposes water by visible light, the valence band holes should be scavenged by a suitable catalyst which promotes oxygen evolution at the expense of photocorrosion:

$$4h^+ + H_2O \xrightarrow{\text{cat}} 4H^+ + O_2 \tag{1}$$

Nakato et al.[4] reported that deposition of a thin layer of gold onto GaP prevented its photoanodic dissolution affording instead water oxidation according to eq 1. It appears, however, that such a reaction is unlikely to occur[5] in view of the high overvoltage for oxygen evolution on Au and the unfavorable energetic position of the valence band of GaP.

In two previous communications we reported on water photolysis with aqueous CdS dispersions.[6,7] Ruthenium oxide, an excellent electrocatalyst for oxygen generation from water,[8] was deposited onto the CdS particles to prevent their photocorrosion which follows the equation

$$2h^+ + CdS \rightarrow Cd^{2+} + S \tag{2}$$

Frank and Honda[9] subsequently observed photoinduced oxygen formation on CdS electrodes using RuO_2, or RuO_2 in conjunction with polypyrrol, to catalyze hole transfer from the valence band of CdS to water. According to a recent report by the same authors, with an improved RuO_2/polymer catalyst,[10] oxygen generation accounts for more than 90% of the photocurrent observed with CdS. By contrast, a sputtered overlayer of RuO_2 on single-crystal CdS was found to be inactive in protecting the semiconductor from photocorrosion.[11] In related photoelectrochemical investigations with Cr-doped $SrTiO_3$ electrodes, Salvador et al. confirmed[12] that RuO_2 could act as a hole-transfer catalyst, accelerating the water oxidation reaction. This is further corroborated in a very recent paper by Noufi,[13] who achieved photoinduced oxygen evolution on n-GaP electrodes covered with a layer of polypyrrole into which RuO_2 had been incorporated.

While the photogeneration of oxygen is easy to detect with n-type semiconductor electrodes, such analysis frequently encounters considerable difficulties when semiconductor dispersions are employed. In the case of aqueous CdS suspensions, photouptake of oxygen is an efficient process[14-20] which is expected to remove rapidly any oxygen produced from the reaction of valence band holes with water. This reaction leads to dissolution of the CdS particles (secondary photocorrosion) whereby H_2O_2[14-16] and sulfate[18-20] are formed simultaneously,[20] eq 3.

$$CdS + 2H^+ + O_2 \xrightarrow{h\nu} Cd^{2+} + H_2O_2 + S \tag{3a}$$

$$CdS + 2O_2 \xrightarrow{h\nu} CdSO_4 \tag{3b}$$

The primary step in both photoreactions is the reduction of oxygen to superoxide by conduction band electrons[15,15]

$$e_{CB}^-(CdS) + O_2 \rightarrow O_2^- \tag{4}$$

Apparently, the phenomena associated with photoinduced uptake of oxygen obscure the primary water oxidation events, rendering their analysis very difficult. In order to avoid these complications, one might resort to open systems[7] where the dispersion is continuously flushed with inert gas during the photolysis. An alternative strategy developed in the present paper is to add an acceptor to the solution which competes with oxygen for conduction band electrons. The advantage of the latter approach is that it allows for a direct analysis of the valence band processes in illuminated CdS dispersions with and without redox catalyst.

Experimental Section

Materials. Cadmium sulfide (purissimum >99.999%), hydrated $RhCl_3$, $RuCl_3{\cdot}H_2O$, and K_2PtCl_6 were purchased from Fluka. All other chemicals were at least reagent grade and used as supplied by the vendor. Deionized water was further purified by Millipore filtration and subsequent distillation from a quartz still.

Catalyst Preparation. (i) **RuO_2/CdS.** The required amount of $RuCl_3{\cdot}H_2O$ was dissolved in 5 mL of H_2O and thoroughly mixed with 1 g of CdS. The slurry was dried in air for 1 h at 80 °C and subequently heated in an oven at 300 °C under air for 1 h. Calculated weight percentage of loading of the CdS particles by RuO_2 varied between 0.5 and 15%. (ii) **Rh_2O_3/CdS.** $RhCl_3{\cdot}H_2O$ (20 mg) was dissolved in 5 mL of H_2O and thoroughly mixed with 2 g of CdS. The slurry was dried at

---

[1] Visiting scientist from the Faculty of Science, Belgrade University, Yugoslavia.

[2] Visiting scientist from the Chinese Academy of Sciences, Lanchow, People's Republic of China.

[3] Gerischer, H. *Pure Appl. Chem.* **1980**, *52*, 2649.

[4] (a) Nakato, Y.; Ohnishy, T.; Tsubomura, H. *Chem. Lett.* **1975**, 883. (b) Nakato, Y.; Abe, K.; Tsubomura, H. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 1002. (c) Nakato, Y.; Tonomura, S.; Tsubomura, H. *Ibid.* **1976**, *80*, 1289.

[5] (a) Wilson, R. H.; Harris, L. A.; Gerstner, M. E. *J. Electrochem. Soc.* **1977**, *124*, 1511. (b) Harris, L. A.; Gerstner, M. E.; Wilson, R. H. *J. Electrochem. Soc.* **1977**, *124*, 1511.

[6] Kalyanasundaram, K.; Borgarello, E.; Grätzel, M. *Helv. Chim. Acta* **1981**, *64*, 362.

[7] Kalyanasundaram, K.; Borgarello, E.; Duonghong, D.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *20*, 987.

[8] Galizzidi, D.; Tantardini, F.; Trasatti, S. *J. Appl. Electrochem.* **1974**, *4*, 57.

[9] Frank, A. J.; Wolkow, R.; Hair, M. L. *J. Phys. Chem.* **1981**, *85*, 4026.

[10] Frank, A. J.; Honda, K. Extended Abstract, Electrochemical Society Meeting, San Francisco, CA, May 1983; p 24, Book of Abstracts, Fifth International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan 1984.

[11] Gissler, W.; McEvoy, A. J.; Grätzel, M. *J. Electrochem. Soc.* **1982**, *129*, 1733.

[12] Salvador, P.; Fernandez, V. M.; Gutierrez, C. *Sol. Energy Mater.* **1982**, *7*, 323.

[13] Noufi, R. *J. Electrochem. Soc.* **1983**, *130*, 2126.

[14] Stephens, R. E.; Ke, B.; Trivich, D. *J. Phys. Chem.* **1955**, *55*, 966.

[15] (a) Harbour, J. R.; Hair, M. L. *J. Phys. Chem.* **1977**, *81*, 1791. (b) *Ibid.* **1978**, *82*, 1397.

[16] Krasnovsky, A. A.; Brin, G. P.; Luganskaya, A. N.; Nikandrov, V. V. *Dokl. Akad. Nauk SSSR* **1979**, *249*, 896.

[17] Harbour, J. R.; Wolkow, R.; Hair, M. L. *J. Phys. Chem.* **1981**, *85*, 4026.

[18] Weber, E. H. *Phys. Status Solidi* **1969**, *36*, 175.

[19] Richardson, D. *Chem. Nachr.* **1886**, *54*, 297.

[20] Meissner, D.; Memming, R.; Kastening, B.; Li, S.; Yesodharan, S.; Grätzel, M., manuscript in preparation.

0002-7863/84/1506-6565$01.50/0

80 °C in air for 1 h and subsequently heated in an oven at 300 °C under air for 5 h. The temperature was subsequently raised for 10 min to 470 °C in order to accomplish complete conversion[21] of $RhCl_3$ into Rh_2O_3 (rate of heating was ca. 20 °C/min). After the mixture was cooled, the CdS/Rh_2O_3 particles were stirred for 30 min in an aqueous solution containing 0.2 M acetic acid (pH 4.5) which was kept at 60 °C. Through this procedure any CdO present initially as a contaminant or formed during the air treatment at elevated temperature is removed from the surface of the CdS particles.[22] Final loading of the CdS powder with Rh_2O_3 was 0.5%. The BET surface area of the CdS/Rh_2O_3 particles was determined as 1.8 m^2/g.

Apparatus. Illuminations were performed with a 660- or 450-W xenon lamp whose infrared and UV output was removed by means of a water jacket and a 420-nm cut-off filter, respectively. Solution (18–20 mL) was contained in the inner part of a double-walled cylindrical Pyrex glass vessel whose outer compartment was continuously flushed with water from a thermostat to maintain the temperature of the dispersion at 25 °C. Total volume of the cell was 30 mL. A few irradiations, in particular the O_2 uptake experiments, were performed with 10-mL solutions contained in a single-walled Pyrex vial with a head space of ca. 4 mL.

Oxygen concentration in solutions was continuously monitored by a Clark-type membrane electrode (Yellow Springs Instruments, YSI Model 53) connected to a potentiostat. Alternatively, analysis of the oxygen content in the gas phase was carried out at regular intervals by gas chromatography. A Poropack 5-Å molecular sieve column was used in conjunction with a Gow-Mack thermal conductivity detector. Argon served as a carrier gas and was also used to deaerate the solution prior to photolysis. In order to avoid ambiguities in the oxygen analysis resulting from air leakage,[23] the irradiation cell with electrodes and recorder or gas chromatograph were all mounted in a glovebox which was kept free from air by continuously flushing with Ar.[24] This combined procedure of oxygen analysis proved to be reliable and sensitive. Performance of the experiments under unaerobic conditions allows furthermore the avoidance of misinterpretation of the results due to air contamination.

The oxygen results were further substantiated by performing photolysis with CdS/Rh_2O_3 dispersions in H_2O^{18} (Monsanto Research Corp., Miamisburg; ^{18}O isotope content ca. 95%). In this case the solution volume was reduced to 4 mL, contained in a round flask of 15-mL volume. Prior to irradiation, the system was deaerated by flushing with Ar. Gas analysis was carried out by mass spectrometry on a ZAB-2F double-focusing instrument having reverse geometry coupled on-line with a PDP-11/34 computer. The instrument settings were as follows: source temperature 200 °C, accelerating voltage 8 kV, emission current 100 μA, electron energy 70 eV, and mass resolution 2500. The reaction vessel was fitted to the all-glass-heated inlet system (AGHIS) of the instrument. The aqueous solution was frozen in liquid nitrogen, and the supernatant gas was introduced into the AGHIS reservoir to a source pressure of 10^{-8} torr. The mass spectrometer was then scanned repetitively over the mass range 27–38 by sweeping the magnetic sector with a microprocessed digital scan unit. Thirty scans of 4 s were taken by the computer and averaged. The background of the mass spectrometer was free of any signal at *m*/*z* 36 before introducing the sample.

Cadmium and platinum ion analysis was carried out by atomic spectroscopy by using a Perkin-Elmer ICP/5000 inductively coupled plasma system equipped with a Cd lamp. Irradiated dispersion were acidified to pH ~5 and stirred for 2 h to dissolve any Cd^{2+} precipitated as hydroxide under the alkaline conditions employed in the photolysis experiments. The CdS particles were subsequently removed by centrifugation and the supernatant subjected to Cd^{2+} analysis. Blank experiments established that Cd^{2+} ions generated under the experimental conditions could be quantitatively detected in this manner and allowed also to determine the background Cd^{2+} concentration present in these dispersions.

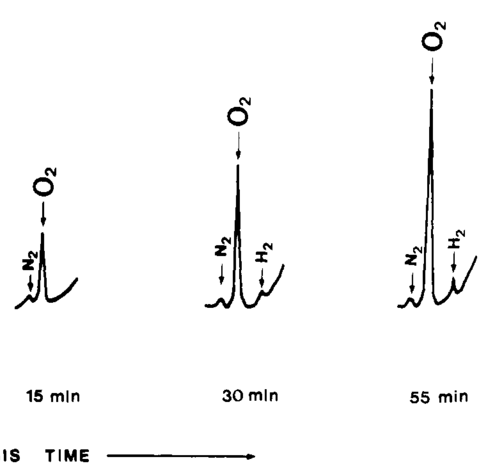

Figure 1. Visible light induced oxygen evolution from CdS/Rh_2O_3 (0.5%) suspensions. Oxygen analysis was performed by GC analysis of the gas phase present in the head space above the CdS/Rh_2O_3 dispersion. Irradiation cell and detector were placed in a glovebox that was continuously flushed with Ar. Solution was also deaerated by flushing with Ar. Chromatograms were taken 15, 20, and 55 min after beginning of the irradiation. Conditions: 25 °C, pH 13 (0.1 N NaOH), 10^{-2} M K_2PtCl_6, CdS/Rh_2O_3 concentration 10 mg/mL. Light source: 600-W Xe lamp with 420-nm cut-off filter, solution contained in a double-walled Pyrex cell.

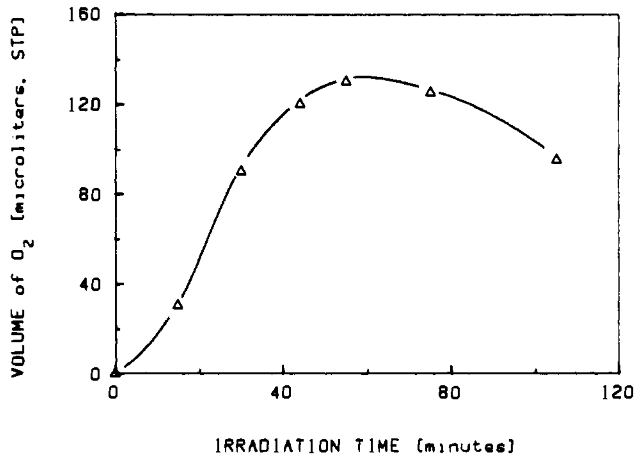

Figure 2. Visible light induced oxygen evolution from CdS/Rh_2O_3 suspension. The amount of O_2 detected in the gas phase (in μL STP) is plotted as a function of irradiation time. Conditions are in Figure 1.

Results

Figure 1 shows three gas chromatograms obtained from the visible light illumination of CdS/Rh_2O_3 suspensions in water in the presence of 10^{-2} $PtCl_6^{3-}$ as electron acceptor. Solution volume was 18 mL (head space in the cell, 12 mL), the CdS concentration was 10 mg/mL, and the pH was adjusted to 13 with NaOH. Irradiation was performed in the glovebox under an Ar atmosphere with use of the 600-W Xe lamp as a light source. The three chromatograms demonstrate clearly that significant amounts of oxygen are produced under illumination. Volumes of O_2 generated after 15, 30, and 55 min are 40, 90, and 130 μL (STP), respectively. The signal for N_2 remained very small throughout the photolysis, indicating that the contribution of air contamination can be neglected. Furthermore, the chromatograms reveal that in the later stage of the photolysis small amounts of H_2 (2–3 μL) are formed concomitantly with O_2.

Figure 2 shows a plot of the oxygen volume ($F(O_2)$) determined by GC analysis as described above as a function of illumination time. $V(O_2)$ grows continuously up to ca. 1 h when a plateau is reached. Thereafter slow photoconsumption of O_2 becomes visible.

---

[21] Ivashentsev, Ya. I.; Timonova, R. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1966**, *11*, 1173.

[22] Reber, J. F.; Meier, K.; Bühler, N. International Conference of Solar Energy Conversion, 4th, Jerusalem, Israel, Aug. 8–13, 1982; Abstract 252–254. We thank Dr. Reber for communicating to us these results prior to publication.

[23] Photolysis vessels are frequently equipped with a rubber septum, allowing for withdrawal of gas samples by a microsyringe during irradiation and subsequent GC analysis. These septa are sometimes made out of materials through which O_2 diffuses more rapidly than N_2. While these diffusion processes are very slow, they can give problems with the O_2 analysis by GC technique if the amount of O_2 to be detected is smaller than or comparable to that which leaked across the membrane. In this case, the N_2/O_2 peak ratio obtained from injection of air cannot be safely used to correct for the leakage since the gas mixture after penetrating through the septum has a higher O_2 content than air. We are grateful to Mr. Dieter Meissner, University of Hamburg, West Germany, and to one referee for alerting us to this possibility and for suggesting the present setup which avoids ambiguities arising from air leakage.

[24] We are grateful to Mr. Dieter Meissner, University of Hamburg, West Germany, and Dr. Detlef Bahnemann, Hahn-Meitner-Institute, West Berlin, for their participation in the initial stage of these experiments.

In order to test whether the O_2 detected by GC technique results from water oxidation, experiments with H_2O^{18} were performed. CdS/Rh_2O_3 (40 mg) was dispersed in 4 mL of water (^{18}O content 95%), containing 0.1 M NaOH and 10^{-2} M $PtCl_6^{2-}$. The suspension was placed in a 15-mL flask equipped with a ground glass connector and deaerated with Ar. Subsequently, the sample was illuminated with the visible ($\lambda > 420$ nm) light output of the 450-W Xe lamp until ca. 10 μL of O_2 had been formed as determined by gas chromatography. The flask was then attached to the mass spectrometer and analysis of the gas was performed as described in the Experimental Section. A doublet was detected at m/z 36 and a singlet at m/z 34. The components of the doublet were peak-matched, and their exact mass ratio was found to be 1.000 850 which corresponds undoubtedly to ^{36}Ar and $^{36}O_2$ (theoretical value 1.000 850). Their intensity ratio corresponds roughly to a pressure of Ar (buffer gas in the experiment) 1600 times higher than that of $^{36}O_2$. From this result one derives that 7 μL of $^{36}O_2$ (STP) are present in the gas mixture. The signal at m/z 34 can be ascribed to $^{34}O_2$, and its intensity was 3 times smaller than that observed for $^{36}O_2$. Therefore, 2.3 μL of $^{34}O_2$ were present in the gas mixture. $^{36}O_2$ and $^{28}N_2$ resulting from air background were also detected. Small amounts of $^{32}O_2$ produced during photolysis could not be quantitatively assessed since the $^{28}N/^{32}O_2$ peak ratio obtained from air fluctuated by 5%. (Note also that the amount of air detected was so small that its natural content of $^{34}O_2$ and $^{36}O_2$ isotopes could have made no contribution to the m/z 34 and 36 signals obtained from the gas that was generated during photolysis.) Since two water molecules are involved in the generation of one oxygen molecule, the ratio of peak intensities of m/z 36 and 34 is given by[25] $r = p/2(1 - p)$ where p is the fraction of $H_2{}^{18}O$ present in the water used for photolysis. Experimentally, we find $r = 33$ which corresponds to $p = 0.87$. According to the specification given by the vendor, the ^{18}O content of the water employed here is 95% which is in good agreement with the experimental finding.[26] These results leave no doubt that water is the source of the oxygen generated in the visible light photolysis of CdS/Rh_2O_3 dispersions.

We checked whether oxygen generation during illumination of CdS/Rh_2O_3 dispersions in the presence of $PtCl_6^{2-}$ is accompanied by an increase in Cd^{2+} ion concentration. Atomic adsorption spectroscopy was used as an analytical technique since the presence of $PtCl_6^{2-}$ interferes with polarographic analysis. A dispersion of 100 mg of CdS/Rh_2O_3 in 10 mL of water containing 0.1 N NaOH and 10^{-2} M $PtCl_6^{2-}$ was irradiated until 2.5 μmol of O_2 had been produced. The dispersion was then acidified to pH 5 and stirred for several hours in order to dissolve any $Cd(OH)_2$ formed during illumination. The particles were removed subsequently by centrifugation and filtration, and the supernatant was analyzed for Cd^{2+} and Pt. Concentration determined was $[Cd^{2+}] = 1.2 \times 10^{-4}$ M. A blank experiment was run in parallel with an aqueous CdS/Rh_2O_3 dispersion under the same conditions except that this sample was not illuminated. In this solution we detected 1.3×10^{-4} M Cd^{2+} ions. These data show that Cd^{2+} is practically not affected by photoinduced O_2 generation. We can therefore exclude that photocorrosion according to eq 2 makes a significant contribution to the valence band process occurring in illuminated CdS/Rh_2O_3 dispersions. Thus, in the present experiment, if water oxidation and photocorrosion took place with equal probability, the formation of 2.5 μmol of O_2 should have led to an increase in the Cd^{2+} concentration by 5×10^{-4} M which is far above the detection limit of the analytical method used here for Cd^{2+} determination.

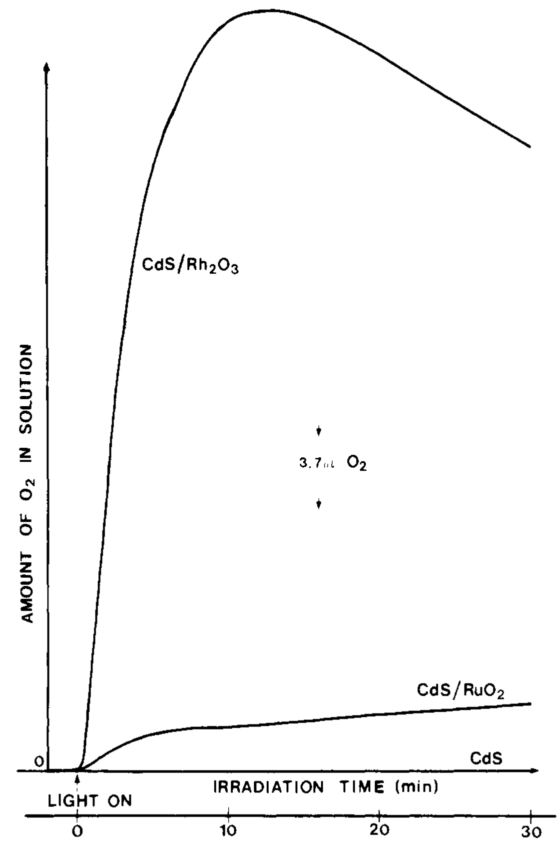

Figure 3. Visible light induced oxygen evolution from aqueous CdS suspensions. The signal output of the Clark sensor, measuring the O_2 content in solution, is plotted as a function of irradiation time. Both thermostated irradiation cell and detection equipment were placed in a glovebox that was continuously flushed with Ar to avoid air contamination. The three curves refer to bare CdS (10 mg/mL), CdS, RuO_2 (1%) (10 mg/mL) and CdS, Rh_2O_3 (0.5%) (10 mg/mL). Other conditions are the same as in Figure 1, except that 0.1 M Li_2CO_3 was present.

The procedure used for the quantitative analysis of Cd^{2+} was checked in the following way: $CdSO_4$ (5×10^{-6} mol) was added to 10 mL of a CdS/Rh_2O_3 dispersion containing 10^{-2} M $PtCl_6^{2-}$ of pH 13. This was stirred in the dark for 2 h and subsequently analyzed in the same was as described above. From the comparison of the calculated with the detected amount of Cd^{2+}, the accuracy of the analytical method was found to be ca. 25%. Therefore, in the photolysis experiment, an increase in Cd^{2+} ion concentration by 3×10^{-5} M could have escaped our detection. This would correspond to a 6% contribution of corrosion according to eq 2 to the total hole current flowing across the CdS/water interface.[27]

It is of interest to compare the activity of Rh_2O_3 with that of RuO_2-loaded CdS particles. In order to avoid interference from the photouptake of oxygen, the efficiency of the catalysts was measured in the initial stage of the photolysis by using a Clark electrode in solution as oxygen sensor. Air contamination was prevented by mounting the irradiation cell as well as the entire detection system in the glovebox which was continuously swept with Ar.

Figure 3 shows oxygen evolution curves obtained from visible light illumination of three different CdS suspensions in the presence of 10^{-2} M $PtCl_6^{2-}$ as electron acceptor. Solution volume was 20 mL (head space in the cell, 10 mL), the CdS concentration was 10 mg/mL, and the pH was adjusted to 13 with NaOH. Electrolyte (0.1 M Li_2CO_3) was added to decrease the solubility of O_2 in the dispersion. Prior to irradiation, the system was deaerated by flushing with Ar. The cell was then closed, the gas stream was turned off, and the dispersion was stirred in the dark for at least 1–2 h until the detector gave a reliable and stable base line. The three curves in Figure 3 reflect the signal output of the Clark sensor monitoring the oxygen content of the solution. For

---

(25) Duonghong, D.; Erbs, W.; Li, S.; Grätzel, M. *Chem. Phys. Lett.* **1983**, *95*, 266.

(26) The ^{16}O content of the solution is somewhat higher than that of the water used to make up the dispersion since ^{16}O is contained on the NaOH and hydration water of K_2PtCl_6 and $H_2{}^{16}O$ is adsorbed on the surface of the CdS particles.

(27) The blank experiment shows that the amount of $PtCl_6^{2-}$ detected is smaller than that added to the solution. A systematic error in the analysis may arise from $PtCl_6^{2-}$ adsorption to the CdS particles. This could affect also the difference in $PtCl_6^{2-}$ concentration between irradiated and nonirradiated solution which cannot be safely used to calculate the amount of Pt deposited.

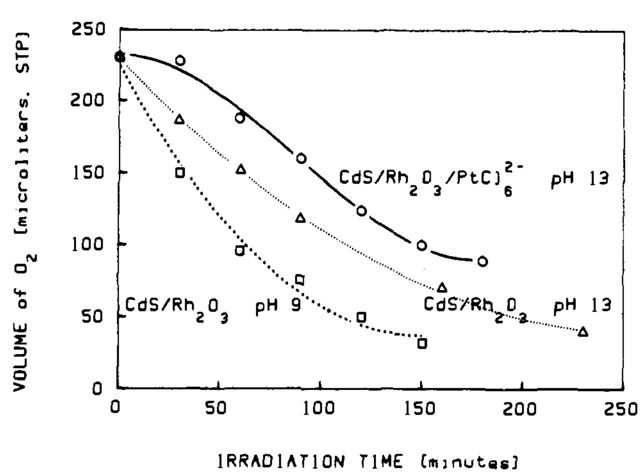

Figure 4. Visible light induced uptake of oxygen by CdS/Rh_2O_3 dispersions. Conditions: pH 13, 10 mg/mL of CdS/Rh_2O_3, solution volume 10 mL contained in a Pyrex vial, room temperature. Light source: 450-W Xe lamp. Solutions deaerated with Ar and subsequently injection of 230 μL of O_2. (□) CdS/Rh_2O_3, pH 9; (△) CdS/Rh_2O_3, pH 13; (○) CdS/Rh_2O_3, pH 13 + 10^{-2} M $PtCl_6^{2-}$.

ease of comparison, they were taken under identical experimental conditions and refer to a similar sensitivity scale of the detector. The signal obtained for dispersions of bare CdS particles is identical with the base line, indicating that no O_2 is produced under illumination. In contrast, the photolysis of RuO_2-loaded CuS suspensions does generate oxygen, the initial rate being 0.6 μL (STP)/min. Strikingly high efficiencies for water oxidation are obtained when CdS/Rh_2O_3 particles are illuminated by visible light. The initial rate of oxygen generation ($r(O_2)$) is here 9 μL/min, i.e., 15 times higher than that obtained with RuO_2, and this rate is achieved with a significantly smaller degree of loading of the CdS particles with redox catalyst.[28]

Note that in the case of CdS/Rh_2O_3, water oxidation occurred at such a rate that the solution became initialy oversaturated with oxygen. Equilibrium is established through release of O_2 in the gas phase, and this effect is responsible for the appearance of a maximum in the O_2 concentration vs. time function in Figure 3.

An estimate for the initial quantum yield of O_2 formation in the CdS/Rh_2O_3 suspension was obtained in the following way: Using the same experimental setup as in Figure 3, oxygen evolution under visible light illumination was measured for a suspension of WO_3 powder (8 g/L) in an aqueous solution of $AgNO_3$ (5×10^{-2} M, pH 4.5). Quantum yield for O_2 formation in the latter system was recently[28] determined as $\phi(O_2) \geq 0.5\%$. The initial rate of O_2 generation in the WO_3/Ag^+ suspension was 2 times lower than that obtained for CdS/Rh_2O_3 in Figure 3. Since CdS and WO_3 have a similar absorption in the visible,[29] we estimate $\phi(O_2) \geq 1\%$ for the initial quantum yield of visible light induced oxygen generation in the CdS/Rh_2O_3 system.

The curve in Figure 2 showed a decline in O_2 concentration at longer illumination time which was ascribed to the photouptake of oxygen by the CdS particles. This effect is examined further in the following experiment. A suspension of 50 mg of CdS/Rh_2O_3 in 5 mL of H_2O is placed in a cylindrical vial closed with a Teflon cap. After deaeration with Ar a volume of 230 μL of O_2 is injected and its consumption under visible light (450-W Xe lamp) illumination is followed by GC analysis. Figure 4 compares data obtained from CdS/Rh_2O_3 dispersions at pH 9 and pH 13 and shows the effect of $PtCl_6^{2-}$ on the O_2 photouptake at the latter pH. CdS/Rh_2O_3 dispersions at pH 9 consume oxygen very rapidly under illumination: 2 h of photolysis suffices to remove practially all of the injected oxygen. Increasing the pH to 13 retards the photoconsumption of O_2. Here, only 60% of the injected O_2 is removed within 2 h. In the presence of 10^{-2} M $PtCl_6^{2-}$ as electron acceptor there is practically no photouptake of O_2 during the first hour of photolysis. Following this induction period O_2 disappears at a rate comparable to that in $PtCl_6^{2-}$-free solution.

Discussion

In the system presently investigated, visible light photons are adsorbed by the CdS particles, producing electron-hole pairs. The role of $PtCl_6^{2-}$ is to scavenge conduction band electrons:

$$4e_{CB}^- + PtCl_6^{2-} \rightarrow Pt + 6Cl^- \qquad (5)$$

This reaction is well-known and has been frequently applied in the past[30] for the photodeposition of platinum onto semiconductor particles. Furthermore, the decrease in $PtCl_6^{2-}$ concentration and darkening of the CdS particles due to the formation of Pt deposits observed during illumination provide clear evidence for the occurrence of this conduction band process. The valence band reaction occurring concomitantly with Pt deposition is either corrosion of the particles (eq 2) or water oxidation (eq 3). The former reaction predominates on bare CdS particles where we have found no evidence for oxygen formation. In contrast, CdS dispersions loaded with RuO_2 or Rh_2O_3 do produce O_2 under visible light illumination. The rate of oxygen evolution is distinctively higher with Rh_2O_3 when compared to RuO_2, indicating that under the experimental conditions employed in this study, i.e., alkaline pH, the former is a better catalyst for water oxidation than the latter. This may appear surprising in view of the known excellent electrocatalytic properties of RuO_2. However, attention is drawn to recent electrochemical studies of Tamura et al.,[31] who compared galvanostatic polarization curves for various noble metal oxide films deposited onto a Ti substrate. In alkaline medium, the best catalytic activity with regard to water oxidation[22] was exhibited by Rh_2O_3. For example, at 100-mV, overvoltage currents observed with this material[31a] were almost an order of magnitude higher than with RuO_2.

Apart from catalytic activity, the nature of the contact formed between the CdS particle and the noble metal oxide deposit could also influence its performance in light induced water oxidation. Formation of a Schottky barrier would be favorable since it would selectively attract holes. In the case of an ohmic contact, the noble metal oxide could act as a recombination center, decreasing the quantum yield of the photoreaction. A barrier height of 0.5 V has been determined for the CdS/RuO_2 junction[11] while the behavior of the CdS/Rh_2O_3 interface has so far not been investigated.

It remains to be explained why in our experiments light-induced oxygen generation ceases at a relatively low degree of conversion of $PtCl_6^{2-}$ into Pt(0) and is followed by oxygen photouptake. In Figure 2 the volume of O_2 attains a maximum at 130 μL which corresponds to ca. 6 μmol. Since reduction of $PtCl_6^{2-}$ occurs concomitantly with water oxidation, the same amount of Pt,[32] i.e., 6 μmol, is deposted onto the CdS particles, giving a loading of ca. 0.7%. These Pt deposits catalyze the reduction of O_2 by conduction band electrons, as has first been observed by Harbour and Hair.[17] As a consequence, the photouptake of oxygen is enhanced once sufficient Pt has accumulated on the CdS particles, and this explains the decline in the oxygen volume in Figure 2 at longer irradiation time.

This explanation is further corroborated by the results in Figure 4 where the photoconsumption of O_2 was separately investigated. In solutions containing $PtCl_6^{2-}$ there is an induction period where the rate of O_2 formation exceeds or equals that of photocon-

---

(28) The loading of CdS with RuO_2 was varied between 0.1 and 15%. Photoinduced O_2 evolution rate increased with RuO_2 content until it reached a plateau at ca. 1% weight ratio between RuO_2 and CdS. Higher loading led to only small improvement in the O_2 output. On an activity per unit weight of catalyst basis 1% loading gave optimum results.

(29) Erbs, W.; Desilverssro, J.; Borgarello, E.; Grätzel, M. *J. Phys. Chem.*, in press.

(30) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 303.

(31) (a) Tamura, H.; Iwakura, Ch. *Adv. Hydrogen Energy* **1981**, *2*, 229. (b) Inai, M.; Iwakura, Ch.; Tomura, H. *Denki Kagaku* **1980**, *48*, 173.

(32) For other pertinent work concerning water oxidation on Rh_2O_3 anodes, in particular by Burke and co-workers, see: Gutmann, F.; Murphy, O. J. In "Modern Aspects of Electrochemistry"; White R. E., Bockris, J. O'M., Conway, B. E., Eds.; Plenum Press: New York, London, 1983; Vol. 15, Chapter 1. Pallotta, C.; De Tacconi, N. R.; Arvia, A. J. *J. Electroanal. Chem.* **1981**, *122*, 367.

sumption. However, after longer irradiation times, photouptake of O_2 always prevails, and this is attributed to the catalysts of reaction 3 by Pt deposits on the CdS particles formed during the photoreaction. At the same time, the Pt deposits also catalyze the formation of H_2 from water and conduction band electrons. This explains the appearance of H_2 in the gas chromatograms in Figure 1 after longer irradiation times.

Conclusions

Oxygen is generated when suspensions of CdS loaded with noble metal oxides are illuminated by visible light in the presence of an acceptor for conduction band electrons. An important result of the present investigation concerns the high catalytic activity of Rh_2O_3 in promoting water oxidation by valence band holes: Under alkaline condition the initial quantum yield for O_2 formation observed with CdS/Rh_2O_3 exceeds that of CdS/RuO_2 by a factor of 15.

A characteristic feature of CdS suspensions is rapid photoconsumption of oxygen involving reduction of O_2 by conduction band electrons,[15] and this was shown to interfere with O_2 detection. As was suggested by Harbour et al.,[17] a similar reaction is expected to take place also in water cleavage systems when the photolysis is performed in a closed vessel over long periods of time without intermittent removal of gaseous products. Under such conditions the formation of a gaseous mixture of H_2 and O_2 in a 2:1 M proportion is unlikely to occur and one would expect to detect, apart from hydrogen, the products arising from the photouptake of O_2 by the CdS particles. A detailed analysis of these products will be given in a subsequent paper.[20] The present study was undertaken to identify unambiguously the valence band processes in illuminated CdS suspensions loaded with highly active water oxidation catalysts and to compare their efficiency in promoting oxygen generation.

Acknowledgment. This work was supported by a grant from the Gas Research Institute, Chicago, IL (subcontracting office: Solar Energy Research Institute, Golden, CO). N.M.D. thanks the Yugoslavian government for a traveling stipend. L.S. acknowledges financial help from the Academy of Sciences of the People's Republic of China. We express our deep gratitude to Dr. Daniel Stahl for carrying out the mass spectrometry experiments which were of crucial value for the correct interpretation of our photolysis results and to Professor Tino Gäumann for allowing us to use this sophisticated instrumentation.

Registry No. CdS, 1306-23-6; RuO_2, 12036-10-1; Rh_2O_3, 12036-35-0; $PtCl_6^{2-}$, 16871-54-8; O_2, 7782-44-7; H_2O, 7732-18-5; $H_2{}^{18}O$, 14314-42-2.

Cation Radical Diels–Alder Reaction of 1,3-Butadiene: A Two-Step Cycloaddition

G. S. Groenewold and M. L. Gross*

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588. *Received August 29, 1983*

Abstract: The structure of the ion–molecule adduct produced in the reaction of 1,3-butadiene cation radical with neutral 1,3-butdiene has been investigated by collisionally stabilizing the adduct and then acquiring its collision-activated decomposition (CAD) spectrum by using a tandem mass spectrometer. The CAD spectrum of the adduct changed dramatically depending on the rate of the stabilization. This observation has been interpreted in terms of two distinct structures for the adduct. One which results at a total pressure of 13 mtorr has been identified as 4-vinylcyclohexene cation radical. This identification is based on the similarity of the CAD spectrum of 4-vinylcyclohexene and of the adduct. The second structure, stabilized at higher pressures ($\lesssim$130 mtorr), is a branched, acyclic C_8H_{12} cation radical. The rate constant for the reaction has also been determined. The results of these experiments have been interpreted in terms of a stepwise mechanism for the formation of the 4-vinylcyclohexene cation radical instead of a concerted [4 + 1] cycloaddition mechanism.

1,3-Butadiene is an important molecule from a mechanistic viewpoint because it is the simplest diene component possible in a Diels–Alder cycloaddition. In fact, the reaction of neutral butadiene has served as a model for investigation of the cycloaddition.[1-4] Two mechanistic alternatives for the thermal reaction are a one-step, concerted process and a two-step, nonconcerted one, in which acyclic octa-1,7-dien-3,6-diyl diradicals have been proposed as intermediates. Several studies have focused on comparing the heat of formation of such diaradicals with the heat of formation of the transition state of the Diels–Alder dimerization.[1] The mechanism of the reaction has also been probed by using deuterium labeling[2] and stereochemical[2] and computational[3] methods and by measuring the activation volume of the reaction.[4]

A diradical intermediate in the thermal Diels–Alder reaction cannot be unequivocally excluded. It is known that similar diradicals serve as intermediates in the formation of 1,2-divinylcyclobutanes, which are products of the photochemical dimerization of butadiene.[5] The existence of an analogous acyclic radical cation species as an intermediate in the cation radical cyclization reaction is a reasonable possibility. The diradical intermediates characteristic of butadiene plus butadiene neutral chemistry are transitory and difficult to observe. In contrast, it may be possible to observe a cation radical intermediate in a gas-phase, ionic reaction by collisionally stabilizing it in a conventional high-pressure mass spectrometer source, provided the lifetime of the intermediate is on the order of 1–10 μs.

Several examples of solution-phase cycloaddition reactions involving a cation radical partner have been reported recently by

---

(1) (a) Berson, J. A.; Dervan, P. B. *J. Am. Chem. Soc.* **1973**, *95*, 267. (b) Doering, W. von E.; Franck-Neumann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833. (c) Benson, S. W. *J. Chem. Phys.* **1967**, *46*, 4920.

(2) (a) Stephanson, L. M.; Gemmer, R. V.; Current, S. *J. Am. Chem. Soc.* **1975**, *97*, 5909. (b) Berson, J. A.; Malherbe, R. *J. Am. Chem. Soc.* **1975**, *97*, 5910.

(3) (a) Jug, K.; Kruger, H. W. *Theor. Chim. Acta* **1979**, *52*, 19. (b) Yves, J. *Quantum Theory Chem. React.* **1979**, 1, 53. (c) Oliva, A.; Fernandez-Alonso, J. I.; Bertran, J. *Tetrahedron* **1978**, *34*, 2029. (d) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 2338. (e) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190. (f) Burke, L. A.; Leroy, G. *Theor. Chim. Acta* **1975**, *40*, 313. (g) Burke, L. A.; Leroy, G. *Theor. Chim. Acta* **1977**, *44*, 219. (h) Dewar, M. J. S.; Griffin, A. C.; Kirshner, S. *J. Am. Chem. Soc.* **1974**, *96*, 6225. (i) McIver, J. W. *J. Am. Chem. Soc.* **1972**, *94*, 4782.

(4) McCabe, J. R.; Eckert, C. A. *Acc. Chem. Res.* **1974**, *7*, 251.

(5) Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; pp 422–27.

0002-7863/84/1506-6569$01.50/0 © 1984 American Chemical Society