compound and/or pairwise shape descriptor which best fits the high end of the activity data base should probably be chosen. Also, those reference compounds having diverse multiple group substitutions, e.g., $X_3 \neq X_4$ and both $\neq$ H for the triazines, might be preferable. Such compounds cover greater structural diversity and might extend the utility of a correlation with respect to the possible range of group substitutions.

Lastly we conclude this report by pointing out the significance of the work reported here:

Three-dimensional molecular shape descriptors have been defined for a set of Baker triazines which are DHFR inhibitors. A maximum of two shape descriptors, and one physicochemical feature, are needed to explain the variance in DHFR inhibition activity. No compounds in the data base had to be eliminated in the QSAR analysis as outlyers. The QSAR constructed with the use of molecular shape descriptors is superior to that of Silipo and Hansch[18] which is based solely upon physicochemical and substructural features. Hence, our study demonstrates a clear instance where the systematic consideration of three-dimensional molecular geometry is essential to describing biological drug potency.

Note Added in Proof: On January 15, 1980 part of this work was presented for the first time in a seminar at Warner-Lambert Company, Ann Arbor, MI. This author reported the predicted activity of compound 38 ($\log(1/C) = 7.61$ and 7.72, Table VII). Dr. M. L. Black, of Warner-Lambert, was in attendance and noted that compound 38 had been synthesized by Warner-Lambert but never tested for DHFR activity. On February 6, 1980 a sample of compound 38 was sent to this author by Dr. Black. I immediately forwarded the sample to Professor C. Hansch at Pomona College for testing. The observed activity according to Professor Hansch and colleagues, based upon the correction for enzyme species as noted in Table VI, is 7.36. A second QSAR study of bovine and rat liver DHFR inhibition by the 3-position substituted 2,4-diaminotriazines, reported in ref 19, is complete and the results are to be published in *Arch. Biochem. Biophys.* The predicted activity for bovine liver DHFR is 6.58 while the observed value is 6.73 for compound no. 38. These successful predictions give additional support for the reliability of the QSAR reported in this paper and suggest that the QSAR might be used to develop new lead compounds.

Acknowledgment. The theory and corresponding computer programs to calculate the shape descriptors were developed under private funding. The application of the shape theory to the Baker triazines were funded under a contract from the National Cancer Institute (Contract No. N01-CP-75927) and a grant from the National Science Foundation (Grant No. ENV77-24061). The author appreciates helpful discussions with Dr. R. D. Cramer, III of Smith-Kline Laboratories, Dr. R. D. Battershell of Diamond Shamrock Corporation, Dr. J. Y. Fukunaga of Schering-Plough Corporation, Dr. H. Jabloner of Hercules Incorporated, Professor C. Hansch of Pomona College, and members of A.J.H.'s laboratory during the course of this study. The shaded graphics pictures of the molecular fragments shown in Figure 5 were generated by Dr. Nelson Max of Lawrence Livermore Laboratory from supplied atomic coordinates.

Photoassisted Water–Gas Shift Reaction over Platinized TiO_2 Catalysts

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Received April 24, 1980

Abstract: The reaction of gas-phase water with CO (water–gas shift reaction) over platinized, powdered TiO_2 is found to be catalytic under UV illumination. The reaction kinetics has been studied at temperatures from 0 to 60 °C. At 25 °C, the reaction is zero order both in CO and H_2O when $p_{CO} \geq 0.3$ torr and $p_{H_2O} \geq 5$ torr and the activation energy is 7.5 kcal/mol. The wavelength dependence of the reaction rate shows a cut-off near, but slightly below, the band gap of TiO_2. The quantum efficiency of the reaction is about 0.5% at 25 °C. A mechanism is proposed which involves the photodecomposition of H_2O over platinized TiO_2.

1. Introduction

Heterogeneous photocatalysis is a relatively new branch of catalysis and in almost all cases semiconductors are used because band-gap photon absorption leads to spatially separated electrons and holes which can be used in oxidation–reduction reactions.[1] Metallized semiconductors have recently appeared which are more effective in some cases than semiconductors alone. For example, Bulatov and Khidekel[2] have reported the photodecomposition of acidified water by using platinized TiO_2 (Pt/TiO_2). Kraeutler and Bard[3] have reported the selective decomposition of liquid acetic acid to methane over illuminated Pt/TiO_2. In the gas phase, Hemminger et al.[4] have claimed the photocatalytic production of methane from CO_2 and gaseous H_2O using a $SrTiO_3$ crystal contacted with a Pt foil.

We have recently begun to investigate the photocatalytic properties of TiO_2 and Pt/TiO_2 and have found that UV-illuminated Pt/TiO_2, but not TiO_2 alone, catalytically decomposes liquid H_2O.[5] Platinized TiO_2 also photocatalyzes the reactions of gaseous H_2O with hydrocarbons,[6] active carbon,[6] and lignite[7] to produce H_2 and CO_2, all of which are thermodynamically unfavorable. We report here another photoassisted reaction over Pt/TiO_2, the reaction of gaseous H_2O with CO (water–gas shift reaction). Although this reaction is not thermodynamically uphill

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(1) See e.g. M. Formenti and S. J. Teichner, *Catalysis* (*London*) *2*, 87 (1979).

(2) A. V. Bulatov and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1902 (1976).

(3) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 2239 (1978).

(4) J. C. Heminger, R. Carr, and G. A. Somorjai, *Chem. Phys. Lett.*, **57**, 100 (1978).

(5) S. Sato and J. M. White, *Chem. Phys. Lett.*, in press.

(6) S. Sato and J. M. White, *Chem. Phys. Lett.*, **70**, 131 (1980).

(7) S. Sato and J. M. White, *Ind. Eng. Chem. Prod. Res. Dev.*, submitted for publication.

0002-7863/80/1502-7206\$01.00/0

($\Delta G° = -6.8$ kcal/mol) over illuminated Pt/TiO_2, we believe it does involve the photodecomposition of water. Thus the present study, in addition to having intrinsic interest, serves to promote to our understanding of thermodynamically unfavorable processes over illuminated Pt/TiO_2.

The purpose of this article is to demonstrate that the photoassisted water-gas shift reaction can be catalytically accomplished over platinized titania at room temperature and that a mechanism which is compatible with the data involves the photodecomposition of water. It is not possible to establish clearly many of the molecular level details of this reaction. This awaits further experimentation involving the combination of optical and electron spectroscopic techniques.

2. Experimental Section

TiO_2 (anatase) was obtained from MCB, doped in flowing H_2 for 6 h at 700 °C, cooled in H_2, and stored in a sample vial. Hydrogen was used after passage through a molecular sieve trap at liquid N_2 temperature. Platinized TiO_2 ($\sim$2 wt % Pt) was prepared by the photolysis of hexachloroplatinate dissolved in a Na_2CO_3-acetic acid buffer solution.[8] After photolysis the sample was washed with distilled water until Cl^- could not be detected and then was dried in a desiccator. The BET surface area of Pt/TiO_2 was about 11 m^2/g. Oxygen-18 H_2O (99.3%) was obtained from Prochem. Carbon-13 CO (90%)[9] was used after passing through a liquid N_2 trap.

The apparatus consisted of a vacuum system (base pressure = 1×10^{-7} torr), a gas handling system, a reaction system (180-mL volume), and a gas analysis system, most of which were made of Pyrex glass. The reaction system was equipped with a circulation pump, a quartz reaction cell, and a storage tube of distilled water which was outgassed several times at dry ice temperature.

The catalyst (0.25 g) was spread uniformly on the flat bottom of the reaction cell and outgassed for 3 h at 200 °C. When the water-gas shift reaction was studied, CO was introduced into the reaction system and circulated through the water storage tube to supply water vapor. When low H_2O pressures were needed, the water storage tube was cooled to a temperature at which the desired H_2O vapor pressure was obtained. During reaction the tube was isolated from the reaction system. After the reaction cell temperature was set with a water bath, the catalyst was illuminated with a 200-W high-pressure Hg lamp that was filtered through a quartz cell filled with $NiSO_4$ solution to remove heat. The gas mixture was sampled at various times and after passage through a cold trap at about -110 °C to remove H_2O was analyzed by a mass spectrometer (CEC 21-614). The sensitivity of the mass spectrometer for each gas was calibrated by using a gas mixture of known composition.

3. Results

3.1. Reaction of Gas-Phase H_2O with Doped TiO_2. The hydrogen-doped TiO_2 (without Pt) used in the present experiments reacts with gaseous H_2O to produce H_2 under UV illumination at room temperature. This reaction was accompanied by the production of a small and variable amount of CO_2 which we believe arises from the photodecomposition of adsorbed carbonate. The rate of H_2 formation dropped to zero after a 2-h irradiation, and the maximum amount of H_2 formed was about 3×10^{-7} mol. This reaction was not affected by the presence of CO (i.e., the water-gas shift reaction did not take place) but was completely retarded by the addition of 3×10^{-2} torr of O_2. Hydrogen was also produced when the TiO_2 was heated in gaseous H_2O at temperatures above 200 °C. These results suggest that the H_2 formation arises from the activated and noncatalytic reaction of H_2O with a strongly reduced form of TiO_2 such as Ti_2O_3 or TiO.[10]

3.2. Reaction of H_2O with Pt/TiO_2. When Pt/TiO_2 was illuminated in the presence of gaseous H_2O, H_2 and CO_2 were formed with concomitant formation of a small amount of CH_4. As shown in Figure 1, the use of $H_2{}^{18}O$ instead of ordinary H_2O revealed that a part of the oxygen in CO_2 comes from H_2O. The ratio of ($H_2 + 2CH_4$) to ($C^{18}O_2 + {}^1/_2C^{16}O^{18}O$) is nearly 2:1, suggesting that H_2O is photodecomposed on Pt/TiO_2 and that the oxygen formed reacts with adsorbed carbon and CO. These carbon-containing species are probably present as the result of acetic acid decomposition during the preparation of Pt/TiO_2. The stoichiometric reaction of H_2O with doped TiO_2, described in section 3.1, should not contribute to these results since it will have gone to completion during the catalyst preparation. Oxygen atom exchange between H_2O and CO_2 present originally on TiO_2 may contribute a small amount to the observed $C^{16}O^{18}O$. Hydrogenation of adsorbed carbon will account for the formation of CH_4.

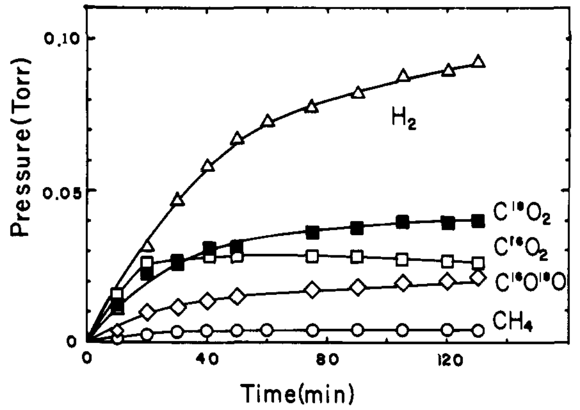

Figure 1. Products of the reaction of $H_2{}^{18}O$ with Pt/TiO_2 under UV illumination ($p_{H_2{}^{18}O} \simeq 24$ torr).

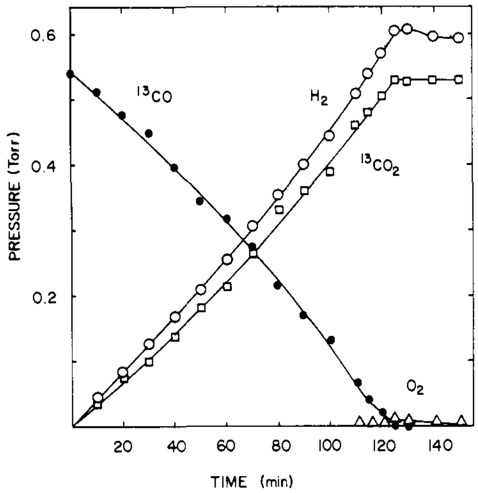

Figure 2. Time course of the water-gas shift reaction over illuminated Pt/TiO_2 at 25 °C ($p_{H_2O} \simeq 24$ torr).

From Figure 1 the maximum yield of H_2 is certainly larger than 0.09 torr (8.7×10^{-7} mol). This is a factor of 3 larger than the maximum H_2 yield found for TiO_2 and suggests that the addition of Pt increases the activity for H_2 production perhaps through a reaction pathway involving the decomposition of water.

If the photodecomposition of H_2O is indeed involved, H_2 should be continuously formed by the addition of some material such as CO, which has a strong affinity for oxygen and forms a nonreactive product such as CO_2. On this basis we tested for, and found, catalytic activity for the water-gas shift reaction on Pt/TiO_2.

3.3. Water-Gas Shift Reaction. General Features. Figure 2 shows a typical time evolution of the water-gas shift reaction over UV-illuminated Pt/TiO_2 at 25 °C. Carbon-13 CO (0.6 torr total, 0.54 torr ^{13}CO) was used in order to discriminate against the CO_2 yield that occurs in the absence of CO(g) (see Figure 1). The water pressure was 24 torr. When the isotopic purity of CO (90% ^{13}C) is taken into account, the stoichiometry of the shift reaction is well satisfied: $-\Delta p_{CO} = \Delta p_{CO_2} = \Delta p_{H_2}$. In the dark, the reaction rate was very slow at room temperature and, at 60 °C, its contribution was only 0.6% of the photoprocess. According to Figure 2, the production of H_2 proceeds with no marked loss of activity until the carbon monoxide is consumed. Once the CO(g) is gone, however, the activity drops sharply to zero. In fact the H_2 pressure passes through a maximum, indicating that some H_2 is consumed

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[8] B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 4317 (1978).

[9] We thank Dr. T. N. Taylor of Los Alamos Scientific Lab for a sample of ^{13}CO.

[10] D. R. Kennedy, M. Ritchie, and J. Mackenzie, *Trans. Faraday Soc.*, **54**, 119 (1958).

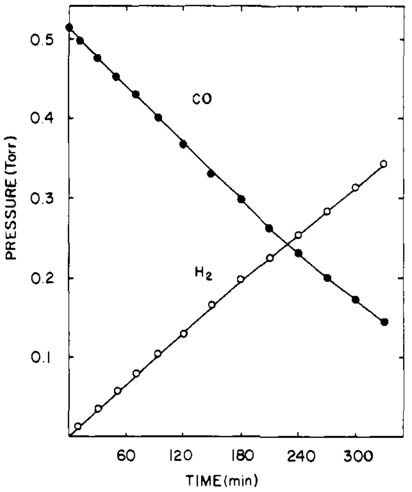

Figure 3. Time course of the photoassisted water-gas shift reaction over Pt/TiO$_2$ at 0 °C. Plots of CO$_2$ are omitted as they almost overlap on the plots of H$_2$ ($p_{H_2O} \simeq$ 5 torr).

in the latter stages of the experiment summarized in Figure 2. In this case the maximum amount of H$_2$ is 5.8 × 10^{-6} mol (1.3 × 10^{18} molecules m^{-2} of catalyst).

As shown in Figure 2, a small amount of O$_2$(g) appears as the pressure of CO drops below 0.06 torr. This pressure gradually increases at the end of reaction and then abruptly jumps to about 10^{-2} torr when the CO pressure drops below 0.01 torr. No other products were detected in this experiment. The same was true for other reaction temperatures between 0 and 60 °C.

Reproducibility. The photocatalytic activity was reproducible in a series of runs when the reaction was stopped and the system evacuated before the CO pressure dropped below about 0.1 torr. If the reaction proceeded to completion, as in Figure 2, an activity increase was sometimes observed upon repeating the reaction after evacuation for only a few minutes. Outgassing for extended periods, even at room temperature, restored the activity to a reproducible value. In our experiments reproducible and stable activity was achieved after any experiment by outgassing at 150 °C for 1 h.

Pressure Dependence at 25 °C. Figure 2 shows that the rate of the photoassisted water–gas shift reaction is almost constant until the pressure of CO falls to about 0.3 torr. Over this range there is a zero-order dependence of the rate on CO pressure. Since the pressure of H$_2$O (24 torr) is much higher than the CO pressure (0.6 torr), the effect of its change during the reaction is negligible. The reaction accelerates slightly as the CO pressure drops below 0.3 torr, indicating a slightly negative order in p_{CO} between 0.3 and 0.1 torr. Near completion the rate slows as the CO pressure drops, implying a positive order in p_{CO}. These qualitative dependences were confirmed in a series of experiments utilizing initial CO pressure from 0.1 to 0.6 torr.

A slight increase in the initial rate (10–20%) was observed when the H$_2$O pressure was reduced from 24 torr to about 5 torr while the initial CO pressure was fixed at about 0.6 torr. The reaction is, therefore, almost zero order in H$_2$O pressure.

Temperature Dependence. Figure 3 shows the time dependence of the reaction at 0 °C. The reaction rate is nearly constant over the entire pressure range observed though a slight decline is observed as the CO pressure drops below 0.25 torr. The consumption of CO exceeds slightly the formation of H$_2$ probably due to CO adsorption on the catalyst during the reaction. The CO$_2$ production rate (not shown) equals the H$_2$ production rate.

At 60 °C (Figure 4) the time evolution is qualitatively like that at 25 °C: an initial constant rate followed by an acceleration at intermediate CO pressures and a retardation at the end of the reaction. However, the CO pressure at which the acceleration begins is higher than that in the reaction at 25 °C. The decline of the rate is not due to a loss of the photocatalytic activity of Pt/TiO$_2$ because the initial rate was reproduced in the next run. When the initial pressure of CO was reduced to 0.5 torr, the rate accelerated earlier than in Figure 4 and the retardation period became shorter. The reaction course at 40 °C showed a pattern intermediate between those at 25 and 60 °C.

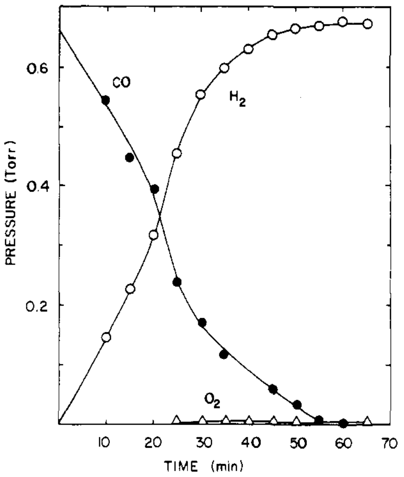

Figure 4. Time course of the photoassisted water–gas shift reaction over Pt/TiO$_2$ at 60 °C. Plots of CO$_2$ almost overlap on those of H$_2$ ($p_{H_2O} \simeq$ 24 torr).

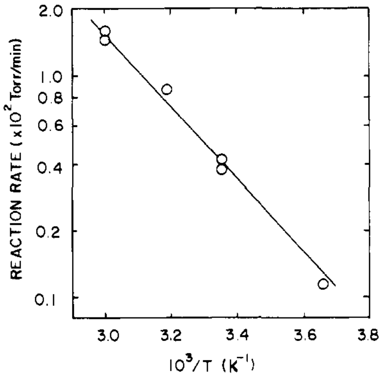

Figure 5. Arrhenius plot of the rates of photoassisted water–gas shift reaction over Pt/TiO$_2$ [p_{CO} = 0.5–0.6 torr, $p_{H_2O} \simeq$ 24 torr (~5 torr at 0 °C)].

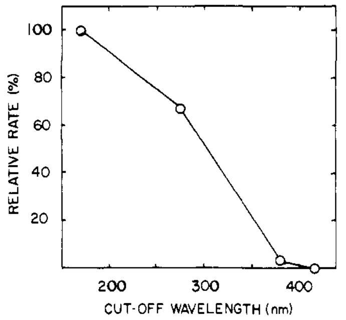

Figure 6. Effects of cutoff filters on the rate of photoassisted water-gas shift reaction over Pt/TiO$_2$ at 25 and 60 °C ($p_{H_2O} \simeq$ 24 torr, p_{CO} = 0.5–0.6 torr).

Figure 5 shows an Arrhenius plot of the reaction rates for temperatures from 0 to 60 °C in the region where the reaction takes place at a constant rate. The activation energy is 7.5 kcal/mol, which is about the same as that estimated for the photoassisted decomposition of liquid water (~5 kcal mol^{-1}).[5]

Wavelength Dependence. The wavelength dependence was qualitatively measured by using three cutoff filters: a commercial UV cutoff filter (415-nm cutoff), a Plexiglass filter (3 mm thick, about 380-nm cutoff), and a Pyrex glass filter (3 mm thick, about 275-nm cutoff). As seen from Figure 6, the 415-nm cutoff filter completely retarded the reaction while the Plexiglass and Pyrex filters suppressed the rate to 4 and 67%, respectively. There was no difference in the wavelength dependence at 25 and 60 °C.

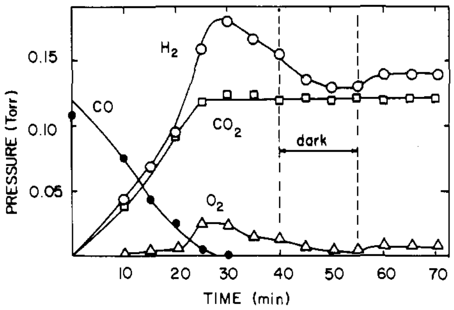

Figure 7. Formation of O_2 during the photoassisted water-gas shift reaction over Pt/TiO_2 at 25 °C ($p_{H_2O} \simeq 24$ torr).

Formation of O_2. The formation of O_2 during the water-gas shift reaction is surprising in the sense that it is not favored thermodynamically. The fact that it is formed may help in understanding the mechanism of the photoassisted water-gas shift reaction over Pt/TiO_2.

Typical pressure vs. time curves for CO, H_2, CO_2, and O_2 are shown in Figure 7. The amount of O_2 is very small (less than 5×10^{-4} torr) and almost constant in the region where the reaction takes place at a constant rate. After the shift reaction accelerates, O_2 gradually increases and then maximizes rather abruptly as CO drops below 0.01 torr. At the same time, the H_2/CO_2 ratio deviates sharply from unity and the excess of H_2 over CO_2 is about twice the amount of O_2 formed, suggesting the decomposition of H_2O. The back-reaction occurs readily over Pt, and Figure 7 suggests that the rate of this process increases when the CO pressure drops below 10^{-3} torr. The H_2 consumption rate observed here is much lower than the H_2 oxidation rate on a Pt/TiO_2 surface not exposed to CO.[5] As shown in Figure 7, the rate becomes a little faster after the light is turned off and turning the light source back on produces small amounts of O_2 and H_2. This O_2 formation pattern was reproducible although the quantitative amounts of O_2 produced in each region are sensitive to the activity of Pt/TiO_2, the reaction temperature and the initial CO pressure. The maximum amount of O_2 formed ($t \simeq 25$ min in Figure 7) is not exactly reproduced but tends to decrease as the reaction temperature increases, as the activity decreases or as the initial CO pressure is raised.

Preparation Method Dependence. The Pt/TiO_2 prepared from undoped TiO_2 (no H_2 treatment) showed much lower ($\simeq$10%) photocatalytic activity than the Pt/H_2-doped TiO_2 for the water-gas shift and the water decomposition reaction. The activity depends upon the conditions of the H_2 doping of TiO_2 (temperature, time, and a flow rate of H_2). A strongly reduced TiO_2 leads to higher activity but an optimum condition was not established. As doping proceeds, TiO_2 changes color from white to light blue, indicating the production of a reduced form of TiO_2. Preliminary ESCA spectra of the doped and undoped forms revealed no detectable differences. The Pt loading may also affect the photocatalytic activity, but this was not examined in the present study.

4. Discussion

Our experiments show that the photoassisted water-gas shift reaction over Pt/TiO_2 is catalytic when the catalyst is irradiated with band-gap radiation. The reaction may involve photoinduced electronic processes similar to those noted in photoelectrochemical (PEC) cells[11] or photoelectrochemical diodes.[12]

At the $Pt-TiO_2$ junctions formed by deposition of Pt, the valence and conduction bands will be bent upwards, because charge transfer will occur to equalize the Fermi levels of these materials. The extent to which this occurs for our catalyst cannot be readily determined because the doping level of TiO_2 is unknown, because the electronic coupling between TiO_2 and Pt is not known and because the Pt particles are small and not fully characterizable by bulk parameters. Upon irradiation and excitation of an electron into the conduction band of TiO_2, charge separation will compete with hole-electron recombination. Holes will tend to migrate to the $Pt-TiO_2$ interface, and the electrons will migrate away from it. When a photostationary state is reached, the bending of the valence and conduction bands in the semiconductor will be reduced and the electrons and holes can be characterized by quasi-Fermi levels.[11] As a result of these photovoltage effects, we expect (1) that recombination of electrons and holes will become relatively more important than would be expected on the basis of the "dark" energy level diagram, (2) that holes will be found at both the Pt/TiO_2 and the TiO_2/gas interfaces, and (3) that electrons will be captured at the Pt particles. If so, the photocatalyzed processes we have observed here can be described by using the diagram (analogous to a shorted electrochemical cell[13]) shown in Figure 8. In this mechanism, holes come to the TiO_2/gas interface where they react with adsorbed water to form an adsorbed OH radical and a proton. The latter diffuses to the Pt, probably mediated by the physisorbed water that is present, where it is reduced. When CO is present, it reacts with the OH radical to give CO_2 and a hydrogen atom which recombines with other hydrogen atoms at Pt sites. In the absence of CO, the adsorbed OH radical will either react with a second hole to form H^+ and a chemisorbed oxygen atom or two OH radicals will recombine to form H_2O_2. Gas-phase oxygen would then be formed either by recombination of oxygen atoms or by the rapid decomposition of H_2O_2. The back-reaction, $H_2(g) + {}^1/_2O_2(g) \rightarrow H_2O(g)$, occurs readily on Pt[14] and even occurs when liquid water is present,[5] but at a slower rate. Consequently, in the absence of CO no measurable O_2 is evolved. In this case the only way a net amount of H_2 is evolved is to use surface carbon, present on the catalysts as a result of preparative techniques, to scavenge oxygen, and to make CO_2 (see Figure 1).

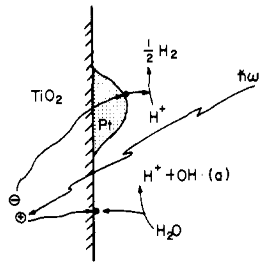

Figure 8. Pictorial Model of the photoinduced redox processes occurring at the Pt/TiO_2 surface.

The above descriptive mechanism is also applicable to the photolysis of liquid-phase water on Pt/TiO_2[5] where the photodissociation rate is more competitive with the back-reaction. There is, however, a problem in view of the fact that the Pt/TiO_2 PEC cell requires an external potential for water decomposition.[11,15] The reason for this requirement is not obvious. There are conflicting views regarding the position of the flat band potential of TiO_2 with respect to the H^+/H_2 redox potential. It has been reported as 50-mV positive[11] and 100-mV negative.[16] In the former case, electrons, arriving at the Pt electrode of a PEC cell must pass an energy barrier to reduce protons to hydrogen (this assumes the pressure is 1 atm). In the latter case, the reaction should occur under short circuit conditions. In either case, overvoltages and other voltage drops will contribute to the inefficiency and to the external potential requirements.

Our results, including those for liquid water,[5] show that this reaction does occur without an external potential when the solid photoactive material involves small Pt particles dispersed on powdered TiO_2. One of the more important differences between our experimental conditions and those in PEC cells is the pressure. The total pressure in our experiments lies between 20 and 25 torr,

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(11) See e.g.: H. P. Maruska and A. K. Ghosh, *Sol. Energy*, **20**, 443 (1978).

(12) A. J. Nozik, *Appl. Phys. Lett.*, **30**, 567 (1977).

(13) A. J. Bard, *J. Photochem.* **10**, 59 (1979).

(14) M. Boudart, D. M. Collins, F. V. Hanson, and W. E. Spicer, *J. Vac. Sci. Technol.*, **14**, 441 (1977).

(15) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, *Proc. Natl. Acad. Sci. U.S.A.* **72**, 1518 (1975).

(16) M. Tomkiewicz, *J. Electrochem. Soc.*, **126**, 1505 (1979).

and the hydrogen pressure never exceeds 0.7 torr. The H^+/H_2 redox potential under these conditions will certainly become more positive with respect to the TiO_2 flat band potential and will allow the reaction to proceed more efficiently. Other differences must also be considered: (1) There will be more surface defects on powdered TiO_2 than on crystalline samples; the attending defect electronic states may be important. (2) The small Pt particles present on our catalyst may have electronic properties different from bulk Pt. (3) Unlike PEC cells, potentially significant[17] direct chemical bonding between Pt and TiO_2 may be present here. The importance of each of these cannot be established on the basis of our data.

Another significant factor in the activity of the solid phase is the reduction of the TiO_2 in the preparation procedure. As noted by Wrighton et al.,[15] this is important in photoelectrochemical cells. One reason is the lower resistivity of the H_2-doped TiO_2 which enhances photoconductivity. We expect this same change in conductivity to be important in our powdered catalysts. Changes in electronic band structure upon creation of oxygen vacancies are also expected, but this can not be examined by kinetic methods. Enhancement of the adsorption of reacting species on the reduced TiO_2 surfaces does not appear to be important.

Focusing now on the water–gas shift reaction, we note that the photodriven dissociation of water is indeed implicated since O_2 evolution is noted (Figures 2, 4, and 7). With the assumption of such a model, the reaction steps probably include (1)–(7). The

$$p^+ + H_2O \rightarrow OH(a) + H^+ \qquad (1)$$

$$p^+ + OH(a) \rightarrow O(a) + H^+ \qquad (2)$$

$$CO(g) \rightarrow CO(a) \qquad (3)$$

$$CO(a) + OH(a) \rightarrow CO_2(g) + H(a) \qquad (4)$$

$$CO(a) + O(a) \rightarrow CO_2(g) \qquad (5)$$

$$H^+ + e^- \rightarrow H(a) \qquad (6)$$

$$2H(a) \rightarrow H_2(g) \qquad (7)$$

intermediates are either denoted in Figure 8 or described in the text that accompanies it. It is not clear whether Pt participates in steps 3, 4, and 5 since it may be covered with H(a) during the reaction, as observed in the hydrogen electrode reaction over Pt dispersed on graphite.[18]

The time course of the water–gas shift reaction consists of three regions: (1) region 1 where the pressure of CO is relatively high and the reaction occurs at a constant rate, (2) region 2 where the reaction gradually accelerates with time, and (3) region 3 where the depression of the rate and the formation of O_2 are observed (Figures 2, 4, and 7).

When the CO pressure is high (region 1), the CO coverage on the catalyst surface would be saturated so that the reaction rate is dependent of the CO pressure. We believe this coverage on Pt inhibits H_2 evolution as observed in the reaction of water with active carbon[19] and lignite[7] over illuminated Pt/TiO_2. The coverage of CO on Pt begins to decrease when the CO pressure is reduced below a certain temperature-dependent value. As a result, the reaction rate accelerates (region 2). When the CO pressure is low (region 3), the diffusion of CO through the layer of physisorbed water on TiO_2 may limit the rate (step 3). As a result the overall reaction rate is suppressed and the coverage of O(a) may increase so that O_2 is produced. Some strongly adsorbed CO would however remain on Pt even after the gaseous CO is consumed and tend to inhibit the reaction of O_2 with H_2. This adsorbed CO may be slowly removed and allow the back-reaction to occur more rapidly (Figure 7).

When the reaction temperature is increased, the amount of CO adsorbed on Pt will drop for a given CO pressure. Accordingly, acceleration of the shift reaction starts at higher CO pressures as indicated in Figures 2–4. The migration of H(a) and O(a) on the catalyst surface, which results in their reaction to form H_2O, may become important at the end of the reaction at 60 °C (Figure 4).

The reaction order with respect to CO pressure is thus explained in terms of the inhibition by CO (zero and negative order) and the CO diffusion (positive order). The zero-order dependence of the rate on H_2O pressure is reasonable since the catalyst surface would be covered with physisorbed H_2O even at relatively low H_2O pressures.

The wavelength dependence of the rate is similar to the wavelength response of the photocurrent in a Pt/W-doped TiO_2 PEC cell studied by Wrighton et al.[15] According to their results, a TiO_2 electrode shows a photocurrent threshold near 400 nm and a saturation near 350 nm, while the onset of W-doped TiO_2 is shifted to shorter wavelengths by nearly 50 nm; H_2-doping and -platinizing TiO_2 may have a similar effect.

The quantum efficiency of the present reaction is low (about 0.5% in region 1 at room temperature). This may be improved by changing the level of H_2 doping and the Pt loading.

Acknowledgment. We thank Mr. B. E. Koel for ESCA analysis of the TiO_2 samples and Mr. S.-K. Shi for his help in the preparation of our experiments. This work was supported in part by the Office of Naval Research.

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