

from the approximately coplanar disposition found in the *cis* isomer, and significantly lengthening the metal-metal distance. This suggests that metal-metal bonding may dictate the conformation in bent bis(fulvalene)-dimetal complexes apart from any possible electronic stabilization from coplanar fulvalene ligands.

- (19) Address correspondence to author at Solar Energy Research Institute, 1536 Cole Blvd., Golden, Colorado 80401.
 (20) Camille and Henry Dreyfus Teacher-Scholar.

James C. Smart,*¹⁹ Barry L. Pinsky

Department of Chemistry and Materials and Molecular
 Research Division of the Lawrence Berkeley Laboratory
 University of California, Berkeley, California 94720

Michael F. Fredrich, Victor W. Day*²⁰

Department of Chemistry, University of Nebraska,
 Lincoln, Nebraska 68588

Received August 4, 1978

On the Photoassisted Decomposition of Water at the Gas-Solid Interface on TiO₂

Sir:

The catalytic nature of the now well-documented photoassisted decomposition of water in photoelectrochemical cells seems to be an established fact, at least on several stable anode materials such as TiO₂ or the alkaline-earth titanates.^{1,2} The amount of gaseous products produced greatly exceeds that which might come from the decomposition (if any) of the surface layers of the electrode. High quantum efficiencies can be achieved and no poisoning of the reaction seems to occur, even after long reaction times.

On the other hand, the catalytic nature of the photoassisted decomposition of water at the gas-solid (GS) interface on simple catalysts, such as pure or doped TiO₂, as reported by Schrauzer and Guth,³ has yet to be established. The efficiency was found much lower than in the photoelectrochemical devices and the reaction actually stopped after a few hours. These authors suggested that this may have been caused by catalysis of the reverse reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$. This could indeed have been responsible because they used small static reactors (200 mg of catalyst in 38-mL capacity vessels).

We have, therefore, studied the photodecomposition of H₂O over TiO₂ in a flow system in order to remove the reaction products from the catalyst completely. Helium, purified by passage over charcoal at liquid nitrogen temperature, was saturated with H₂O at room temperature and flowed over the catalyst (50 cm³ (NTP)/min) for periods up to 6 h. The catalyst (500 mg of anatase; 11.2 m² g) was spread uniformly on a quartz optical plate of area 5 cm² which made up the bottom of a flask which was joined by a standard taper joint to a vacuum-tight flow system. The TiO₂ could be illuminated from below with white light from a 1000-W xenon lamp during the test periods. The exhaust flow was first dried by passing through a liquid N₂ trap and any H₂ or O₂ was subsequently trapped downstream on activated 5A molecular sieve at this temperature. The trapped gases could be released and analyzed by mass spectrometry. The anatase was pretreated *in situ* at 1000 °C in flowing O₂ for 1 h (and consequently partially converted into rutile); it was cooled to 25 °C in wet He. This treatment had been recommended by Schrauzer and Guth as the most efficient for their purposes. Only traces of H₂ were detected, even after 6 h of running in UV light. The O₂ could not be detected unambiguously because of the spectrometer background at *m/e* 32, but certainly a substantial amount (several monolayers) could not have been missed.

We also have studied the hydrogen oxidation reaction over TiO₂, BaTiO₃, and SrTiO₃ in a static recirculation system.⁴ The thermal reaction rate was found to be too slow at 25 °C

by at least one order of magnitude ($<10^{-7}$ mol g⁻¹ h⁻¹) to support the assumption that an equilibrium was reached in the experiments of Schrauzer and Guth, i.e., with hydrogen and oxygen partial pressures of the order of, or <1 Torr and saturating partial pressures of water. Moreover, no rate enhancement by light was found on any of these materials from 400 °C down to room temperature, although enhancement was found for CO oxidation under similar conditions with these systems.

These observations cast serious doubt about the catalytic nature of the process discovered by Schrauzer and Guth. From the particle size given for the TiO₂ sample which they used (2 μ), the specific surface area of the powder may be estimated as ~ 1 m² g⁻¹. Thus, the maximum amounts of H₂ and O₂ observed (5.0×10^{18} and 2.5×10^{18} molecule g⁻¹, respectively) were of the same order as that expected for the photodecomposition of the hydroxylated surface layer⁵ of the material (10^{19} OH m⁻²).

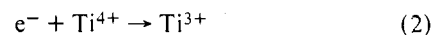
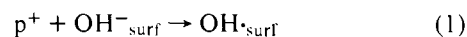
Schrauzer and Guth also showed that hydrogen evolution was inhibited by N₂ in the gas phase and that NH₃ and N₂H₂ were produced instead of H₂, and in higher yields, especially on the iron-doped samples. Assuming again a specific surface area of the order of 1 m² g⁻¹, their highest yield would correspond to about seven monolayers of OH groups. A true surface area determination will be necessary, however, to make these considerations quantitative.

Another thermodynamically "uphill" reaction, namely the reaction of H₂O and CO₂ to form CH₄, has recently been shown to be photoassisted on a SrTiO₃-Pt sandwich.⁶ Remarkably, in this case also, the reaction is poisoned when an equivalent monolayer of methane has been produced.

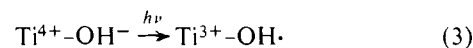
In contrast to these low yields, the photoassisted decomposition of water at the liquid-solid (LS) interface in TiO₂-Pt electrochemical cells occurs with typical rates of $\sim 3 \times 10^{19}$ H₂O molecules decomposed/h on a TiO₂ single-crystal electrode of area ~ 1 cm².^{1,2} This corresponds to a turnover number for each OH group on the electrode surface of the order of 6×10^4 /h, i.e., more than four orders of magnitude higher than at the GS interface.

This large difference in turnover numbers deserves special comment. A fundamental difference between the LS and GS systems is that in the former O₂ and H₂ are produced separately at the oxide anode and at the metallic cathode, respectively, whereas in the latter both are released from the oxide surface. In both types of experiments, however, the primary process going on upon absorption of light in the surface layers may be expected to be the same, i.e., generation of an electron-hole pair, followed by trapping of some of the free carriers.

The following chemistry is written, not because we have firm conviction that it is unique and entirely correct, but rather because it affords a rationale which provides interesting food for thought. For instance, the carriers may be trapped by



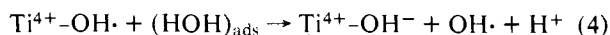
Both the participation of surface OH⁻ groups as hole traps and the identification of Ti³⁺ ions in various environments as donor centers conferring n-type conductivity have been widely proposed. Band to band transition and charge trapping according to eq 1 and 2 could be described together in an equivalent manner.



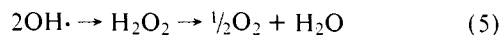
The right-hand member of this equation provides an adequate center for further reaction or for electron-hole recombination.

In the photoelectrochemical (LS) devices, conduction

electrons are transferred continuously in the external circuit to the cathode where H^+ is discharged as H_2 . The Ti^{3+} ion near the surface may therefore be expected to be largely ionized leaving an active chemical species of the type $Ti^{4+}-OH\cdot$. The very high turnover number for O_2 evolution suggests that O_2 is not produced directly from the decomposition of these species, because this would require the rehydroxylation of the surface afterward, which, from what is known about the surface chemistry of many oxides, is a slow process even when a large excess of water is present. Possibly, only physisorbed water is decomposed, according for instance to a charge-transfer process of the type



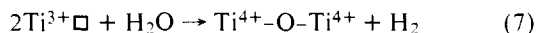
followed by



Although no direct evidence for this mechanism exists to our knowledge, it is significant that OH radicals⁷ and H_2O_2 ⁸ have been detected upon irradiation of TiO_2 in water.

Actually, very little perturbation of the surface structure would be involved with such a model. The surface OH groups of the solid are not decomposed but simply act as intermediates for charge trapping and charge transfer.

On the other hand, at the GS interface, the evidence points to the direct decomposition of the surface OH groups. Boonstra and Mutsaers⁵ have shown that the surface OH groups of TiO_2 can, upon illumination, hydrogenate acetylene and ethylene. As pointed out by Schrauzer and Guth themselves, there seems to be no conceptual difference between this process and the reduction of nitrogen or the formation of H_2 when no reducible substrate is available. Moreover, Schrauzer and co-workers have also shown that the decomposition of several hydroxides is photoassisted in the near-UV.⁹ H_2 is evolved and reducible substrate such as N_2 are reduced, when present. These reactions, however, are not catalytic with respect to the hydroxide and it seems logical to relate them to the photoassisted decomposition of the hydroxylated surface layer on TiO_2 . In addition, the fact that in the GS experiments H_2 is produced on the same surface as O_2 requires that reducing chemical species be generated at some intermediate level near the oxidizing species. Most probably, these reducing species at the surface are derived from the donor centers which, owing to the absence of electron flow in an external circuit, would be much less ionized than in the LS systems. According, to these considerations, O_2 and H_2 could be produced from the following decomposition reactions:



It may be significant that Ti^{3+} -exchanged Zeolite A has recently been shown to yield hydrogen when bathed in water under visible illumination of any wavelength.¹⁰ This suggests that step 7 as well as 3 is also photoassisted.

Compared with the previous model, this reaction scheme requires much more severe surface modifications, particularly for generation (step 6) of the reducing species, $Ti^{3+}\square$.

Moreover, in order to make the process cyclic, hydrolysis of the right-hand member of eq 7 is necessary. As pointed out before, this may be expected to be a slow reaction, and additionally provides a mechanism for irreversible sintering of the oxide.

Some spectroscopic information is available on the nature of the species produced by light on the surface of TiO_2 in GS system. Gravelle et al.¹¹ have shown by ESR spectroscopy that surface Ti^{3+} ions are produced upon evacuation in the dark at moderately high temperature of an hydroxylated surface and that the same species can also be formed by UV irradiation at room temperature. Later, Lo et al.¹² confirmed by various

electron spectroscopic techniques that a Ti^{3+} -rich monolayer is formed under illumination. Furthermore their data suggested that the presence of Ti^{3+} ions on the surface is necessary for the chemisorption of H_2O . Lo et al. did not study the efficiency of the rehydroxylation process in successive rehydration treatments under illumination, but Primet et al.¹³ have shown that the rehydroxylation of a thermally dehydroxylated TiO_2 surface with H_2O vapor was not a truly reproducible process; it was, however, more reproducible for crystalline material than for high surface area amorphous material; the data were taken as evidence of surface reconstruction. We note here that the system should be more stable when TiO_2 is immersed in liquid H_2O than when subjected to alternative dehydroxylation-rehydroxylation cycles, a process known to favor sintering. Although the thermal dehydroxylation of the TiO_2 surface is certainly not identical with its photodecomposition, it seems reasonable to assume that surface reconstruction also occurs in the latter case and that it may be responsible for the loss of activity. Interestingly, it may be this surface chemistry which limits the catalytic efficiency of the gas-solid reactions, rather than electronic considerations.

Acknowledgment. It is a pleasure to acknowledge the support of this research by the National Science Foundation (Grant No. OIP75-21230). In addition, one of us (H.V.D.) is grateful to the Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite of the Centre National de la Recherche Scientifique for the leave of absence in order to carry out this research.

References and Notes

- (1) K. Honda and A. Fujishima, *J. Chem. Soc. Jpn.*, **74**, 355 (1971); *Nature (London)*, **238**, 37 (1972).
- (2) M. G. 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); M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson, and D. S. Ginley, *J. Am. Chem. Soc.*, **98**, 2774 (1976).
- (3) G. N. Schrauzer and T. O. Guth, *J. Am. Chem. Soc.*, **99**, 7189 (1977).
- (4) H. Van Damme and W. K. Hall, unpublished work.
- (5) A. H. Boonstra and C. A. H. A. Mutsaers, *J. Phys. Chem.*, **79**, 2025 (1975).
- (6) J. C. Hemminger, W. J. Lo, and G. A. Somerjai, 176th National Meeting of the American Chemical Society, Miami Beach, Fla., Sept 1978.
- (7) H. G. Völz, G. Kampf, and H. G. Fitzky, *Farbe U. Lack*, **78**, 1037 (1972).
- (8) S. P. Pappas and R. M. Fischer, *J. Paint Tech.*, **46**, 65 (1974).
- (9) S. I. Zones, M. R. Palmer, J. G. Palmer, J. M. Doemeny, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **100**, 2113 (1978).
- (10) S. M. Kuznicki and E. M. Eyring, *J. Am. Chem. Soc.*, **100**, 6790 (1978).
- (11) P. C. Gravelle, F. Juillet, P. Meriaudeau, and S. J. Teichner, *Disc. Faraday Soc.*, **52**, 140 (1971).
- (12) W. J. Lo, Y. W. Chung, and G. A. Somerjai, *Surf. Sci.*, **71**, 199 (1978).
- (13) M. Primet, P. Pichat, and M. V. Mathieu, *J. Phys. Chem.*, **75**, 1216 (1971).
- (14) Centre de Recherche sur les Solides à Organisation Cristalline Imparfaite, 1B, rue de la Férollerie, 45045 Orléans Cedex, France.

H. Van Damme,¹⁴ W. Keith Hall*

Laboratory for Surface Studies, Department of Chemistry,
University of Wisconsin, Milwaukee, Wisconsin 53201

Received March 27, 1979

Computer Retrieval and Analysis of Molecular Geometry.¹ 4. Intermolecular Interactions

Sir:

Intermolecular forces are often described by the sum of isotropic atom-atom potentials² and this approach has been widely used in predicting the packing in molecular crystals.³ However, it has been suggested by several authors⁴ that the heavier p-block elements can form relatively strong directional interactions with nucleophiles for which several terms have been used such as "donor-acceptor interactions",^{4a} "secondary bonding",^{4b} and "incipient nucleophilic attack".⁵ A convincing demonstration of the directional nature was given by Rosenfield, Parthasarathy, and Dunitz⁵ for the system X—S(Y)···N