Photolysis of Water and Photoreduction of Nitrogen on Titanium Dioxide[1]

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Abstract: The photolysis of chemisorbed water on incompletely outgassed TiO_2 powder yields H_2 and O_2 in the molar ratio of 2:1 if conducted under argon. In the presence of molecular nitrogen, O_2 is still formed but the evolution of H_2 is inhibited as chemisorbed nitrogen is reduced to NH_3 and traces of N_2H_4 according to $N_2 + 3H_2O + nh\nu \rightarrow 2NH_3 + 1.5O_2$ and $N_2 + 2H_2O + mh\nu \rightarrow N_2H_4 + O_2$. Iron doping enhances the photocatalytic reactivity of rutile and provides prototypes of solar cells for photochemical ammonia synthesis from N_2 and H_2O.

The photochemical properties of titanium dioxide modifications, i.e., of rutile and anatase, have recieved considerable attention. The *photooxidation* of organic substances in the presence of TiO_2 has been known for a long time as it is responsible for the undesirable darkening of light-exposed TiO_2-paint surfaces.[2] Titanium dioxide also catalyzes the photooxidation of a number of inorganic compounds, e.g., of Hg to HgO[3] or of CN^- to CNO^-.[4] Examples for *photoreductions* have been described as well. Acetylene is converted to a mixture of CH_4, C_2H_4, C_2H_6, and C_3 hydrocarbons when UV irradiated on incompletely outgassed powdered TiO_2. Ethylene is similarly photoreduced, giving rise to CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}.[5] When the TiO_2 was completely outgassed by heating to 500 °C under vacuum, no hydrogenation products were observed. Instead, benzene was formed from C_2H_2 (both photochemically and thermally), and from C_2H_4 only a dimerization product, 1-butene, was obtained.[5] The difference in the behavior between completely and incompletely outgassed TiO_2 was attributed to the loss of chemisorbed H_2O during outgassing which reduces the concentration of surface Ti–OH groups. To explain the photoreduction of the unsaturated hydrocarbons the unlikely suggestion was made[5] that hydrogen atoms are formed during the photolysis reactions. No further mechanistic conclusions could be drawn from these experiments since neither oxygen nor oxygen-containing reaction products were detected in addition to the olefins and alkanes. However, it seemed logical to us to relate these reactions to the well-known photolysis of water on TiO_2 surfaces.[6-8] In reinvestigating the photoreduction of C_2H_2 on TiO_2 we discovered that oxygen was formed as expected but we also noticed that the hydrocarbon product distribution changed when argon was replaced by nitrogen as the protective gas. This suggested that chemisorbed N_2 was reduced under these conditions. The detection of NH_3 and of traces of N_2H_4 by standard methods confirmed this hypothesis and led us to the development of prototypes of *nitrogen reducing solar cells.* The first results of this work will be described in the present paper. In the early experiments pure TiO_2 was employed. In the later experiments, iron-doped TiO_2 was used as this produces more efficient photocatalysts, but a number of results with other metal dopants will also be reported.

Results

Effects of N_2 and of C_2H_2 on the TiO_2-Sensitized Photolysis of H_2O. The photolysis of H_2O has been investigated in electrochemical cells in which the TiO_2 electrode was immersed in H_2O or aqueous solutions of electrolytes.[6-8] Since we were interested in the study of the effects of gases on the photolysis of H_2O a different experimental technique had to be employed. We decided to use TiO_2 powders containing chemisorbed H_2O or surface Ti–OH groups for our experiments, which were placed into irradiation vessels filled with argon, N_2, or other gases. Commercial TiO_2 of 99.9% purity with the particle size 2 μ which consisted essentially of anatase was found to produce traces of H_2 and O_2 if irradiated in the near UV in an atmosphere of argon. Significantly higher yields of H_2 and O_2 were observed using samples of TiO_2 that were subjected to a thermal pretreatment at 1000 °C in air for 1–5 h, followed by rehumidification (exposure to H_2O-saturated argon or N_2; see Experimental Section). During the heat treatment, anatase is converted into rutile; the reaction is essentially complete after 4 h at 1000 °C. However, at this temperature crystal growth is also noticeable, causing a diminution of active surface in addition to increasing loss of surface Ti–OH groups. The optimal heating time was empirically determined to be between 1 and 2 h; this produced samples consisting of mixtures of rutile and anatase, appearing as conglomerates of crystals of 0.1–0.3 μ diameter, as evidenced by scanning electron microscopy. After storage in H_2O-saturated argon at 25 °C for 6 days the water content was on the average between 0.2 and 0.4 wt %. Irradiation of this TiO_2 with UV light emitted from a Hg-arc lamp in glass vessels under *argon* yields H_2 and O_2 from the chemisorbed H_2O in the expected molar ratio of 2:1 as is shown in Table I.

Molecular *nitrogen* at 1 atm of pressure completely inhibits the H_2 formation but has no effect on the yields of O_2. Acetylene also inhibits the H_2 production (see Table I) and since C_2H_2 is known[5] to be photoreduced under these conditions it seemed reasonable to expect that N_2 was photoreduced as well. Analysis of extracts of TiO_2 after UV irradiation under N_2 showed that NH_3 and traces of N_2H_4 were formed. These results were confirmed with $^{15}N_2$-enriched N_2 as the substrate. Although rutile is known[9] to chemisorb N_2 as well as H_2O, the system is complicated as surface hydroxylation and N_2 absorption are strongly dependent on sample pretreatment. The product yields quoted in Table I and the subsequent experiments are not necessarily optimal.

Experiments with Fe-Doped TiO_2. Iron-doped rutile was prepared by heating iron(III) sulfate impregnated anatase to 1000 °C in air. The dissolution of Fe_2O_3 in the TiO_2 lattice accelerates the anatase → rutile conversion as well as crystal growth and produces strongly phototropic samples at concentrations of about 0.2 wt % Fe_2O_3.[10] Table I indicates that the yields of H_2 and O_2 are significantly higher than with undoped TiO_2, at least after 2 h of irradiation. On prolonged irradiation no further yield increases or declines are observed presumably because the reaction of H_2 with O_2 to H_2O is also catalyzed. Both N_2 and C_2H_2 inhibit the H_2 production but have no effect on the yields of O_2; colorimetric determinations revealed that more NH_3 and N_2H_4 were formed than with

Table I. Effects of Nitrogen and of Acetylene on the Photolysis of Water on Powdered TiO_2 and Iron-Doped TiO_2 upon Irradiation with Light Emitted from a 360-W Hanovia Hg-Arc Lamp at 50 °C, TiO_2 Sample Weight 0.2 g, Equilibrated with H_2O Vapor at 25 °C

No.	Conditions	Irradiation time, h	Yields, μmol			
			H_2	O_2	NH_3	N_2H_4
1	Anatase, outgassed at 200 °C, 1 atm Ar	2.0	0.21	0.11	0	0
2	Rutile,[a] 1 atm Ar	1.0	0.45	0.24	0	0
3	Rutile,[a] 1 atm Ar	2.0	0.80	0.39	0	0
4	Rutile,[a] 1 atm N_2	2.0	0.00	0.40	0.50	0.09
5	Rutile,[a] 1 atm N_2[b]	2.0	0.00	0.39	0.52	0.11
6	Rutile,[a] 1 atm N_2 in the dark, 2 h at 50 °C		0.00	0.00	0.01[c]	0
7	TiO_2/0.2% Fe_2O_3,[d] 1 atm Ar	0.5	0.78	0.40	0	0
8	TiO_2/0.2% Fe_2O_3,[d] 1 atm Ar	1.0	1.84	0.90	0	0
9	TiO_2/0.2% Fe_2O_3,[d] 1 atm Ar	2.0	2.32	1.10	0	0
10	TiO_2/0.2% 10 vol % N_2 in Ar	2.0	1.22	1.04	0.55	0.09
11	TiO_2/0.2% 1:1 N_2/Ar at 1 atm	2.0	0.10	0.92	1.15	0.12
12	TiO_2/0.2% 1 atm N_2	2.0	0.02	1.05	1.39	0.15
13	TiO_2/0.2% 1 atm N_2 in the dark, 2 h at 50 °C		0.00	0.05[c]	0.01	0
14	TiO_2[a] 1:1 C_2H_2/Ar at 1 atm	2.0	0.00	0.42	0	0
15	TiO_2/0.2% Fe_2O_3, 1:1 C_2H_2/Ar, 1 atm	2.0	0.00	1.38	0	0

[a] After heating of anatase to 1000 °C in air for 4 h, followed by rehumidification. [b] Substrate was enriched with 20% $^{15}N_2$; yields determined mass spectrographically. [c] Probably background. [d] Mixture of 23% rutile and 77% anatase after 1 h of heating to 1000 °C.

Table II. Photoreduction of Molecular Nitrogen on Powdered TiO_2 and Iron-Doped TiO_2 under Different Conditions, Light Source 360-W Hanovia Hg-Arc Lamp, Weight of Titania Photocatalyst 0.2 g (Also See Experimental Section)

No.	Variable and conditions	Yields, μmol[b]		Reaction time, h
		NH_3	N_2H_4	
	Iron content of TiO_2[a]			
1	0.0 wt % Fe_2O_3, $T = 40$ °C, N_2 1 atm	1.75 ± 0.5	0.12 ± 0.05	3
2	0.05	2.8 ± 0.7		3
3	0.10	4.4 ± 2.0		3
4	0.20	6.0 ± 2.5	0.19 ± 0.07	3
5	0.30	5.5 ± 2.0		3
6	0.40	5.4 ± 2.0		3
7	0.50	3.8 ± 1.5	0.15 ± 0.05	3
8	1.00	2.5 ± 1.0		3
9	100 wt % Fe_2O_3 (α modification)	0.6 ± 0.2	<0.05	3
	Reaction time			
10	0.20 wt % Fe_2O_3 $T = 40$ °C, N_2 1 atm	1.5	0.08	1
11		3.4	0.11	2
12		5.9	0.18	3
13		6.6	0.14	4
	Temperature			
14	0.20 wt % Fe_2O_3 $T = 30$ °C	4.8	0.12	3
15	50 °C	6.0	0.14	3
16	80 °C	2.0	<0.05	3
17	120 °C	0.55	<0.05	3
18	180 °C	0.42	<0.05	3
	Gas phase			
19	0.20 wt % Fe_2O_3 $T = 40$ °C Ar 1 atm	0.01	0	3
20	N_2 0.3 atm	1.53	Tr	3
21	N_2 0.6 atm	4.35	0.09	3
22	N_2 1.5 atm	6.95	0.18	3
23	Air 1.0 atm	1.23	Tr	3
24	1:1 N_2/H_2 1.0 atm	3.45	0.11	3

[a] Iron doped TiO_2 was prepared by adding iron(III) sulfate solution to TiO_2 in the anatase modification and heating to 1000 °C for 1 h. Rutile content in samples 1-8 as determined by x-ray analysis: 1, 10%; 2, 12%; 3, 18%; 4, 23%; 5, 35%; 6, 43%; 7, 52%; 8, > 98%. Average H_2O content: 0.30 wt % estimated from weight loss on heating for 2 h at 1000 °C. [b] Yields of N_2H_4 are more variable than those of NH_3 as N_2H_4 decomposes and/or is reduced on prolonged irradiation under the experimental conditions chosen.

undoped TiO_2 (Table I) and that no reduction of N_2 occurred in the dark under otherwise identical conditions.

Factors Influencing Photoreduction. Iron Content of TiO_2. Table II summarizes the results of N_2-photoreduction experiments under various conditions. As the Fe content of TiO_2 is increased above 0.2 wt % Fe_2O_3 the photocatalytic efficiency declines. Such samples of doped TiO_2 contained a greater proportion of rutile; at 1 wt % Fe_2O_3 anatase was no longer detectable by x-ray crystallographic methods; during the 1 h heat treatment at 1000 °C, well-formed single crystals of rutile reaching 5 μ in length had formed. The comparatively low activity of this sample (no. 8 in Table II) thus is at least in part caused by diminished active surface as compared to the 0.2 wt % Fe_2O_3-doped sample which was not fully converted into rutile and whose crystallite diameter was between 0.5 and 1 μ. Experiment no. 9 in Table II reveals that powdered H_2O-equilibrated α-Fe_2O_3 also produces some NH_3 on UV irradiation in the presence of N_2.

Reaction Time. The yields of NH_3 increase at least during 4 h of UV irradiation of 0.2 wt % Fe_2O_3-doped TiO_2 (experiments no. 10-13 in Table II).

Temperature. The highest yields of NH_3 and N_2H_4 were

Table III. Effects of Thermal Pretreatment and Rehumidification on the Photocatalytic Activity of 0.2 wt % Fe_2O_3-Doped TiO_2, Sample Size 0.2 g, Irradiation Temperature 40 °C, Nitrogen Pressure 1 Atm. Yields Measured after 3 h of UV Irradiation

No.	Duration of 1000 °C heat pretreatment, h	Rutile: anatase	Method of Cooling		
			In wet N_2	In dry N_2	Under vacuum
				Ammonia, μmol	
1	1	23:77	6.9	3.8	3.6
2	2	30:70	6.5	3.6	3.0
3	3	45:55	4.3	2.9	2.4
4	4	85:15	2.6	2.3	1.0
5	5	100	2.5	2.0	1.0
6	6	100	2.4	1.8	0.8

Table IV. Yields of Ammonia and of Hydrazine from Nitrogen on Exposure of Undoped and Fe-Doped TiO_2 to Intermittent Sunlight at Temperatures between 25 and 35 °C

No.	Conditions and catalyst[a]	Yields, μmol	
		NH_3	N_2H_4
1	TiO_2, 1 atm Ar	0	0
2	TiO_2, 0.5 atm N_2	0.74	0.05
3	TiO_2, 1 atm N_2	1.55	0.17
4	TiO_2/0.05 wt % Fe_2O_3, 1 atm Ar	0	0
5	TiO_2/0.05 wt % Fe_2O_3, 1 atm N_2	3.20	0.09
6	TiO_2/0.2 wt % Fe_2O_3, 1 atm N_2	4.98	0.12
7	TiO_2/0.2 wt % Fe_2O_3, 1 atm air	1.89	0.07
8	TiO_2/0.5 wt % Fe_2O_3, 1 atm Ar	0	0
9	TiO_2/0.5 wt % Fe_2O_3, 1 atm N_2	4.65	0.19
10	TiO_2/0.5 wt % Fe_2O_3, 1 atm air	2.0	0.11

[a] Sample weight 0.2 g. All photocatalysts were heated for 1 h at 1000 °C in air and stored in H_2O-saturated N_2-filled containers. Rutile/anatase ratios for samples 1-3, 10/90; 4, 5, 10/90; 6, 7, 15/85; 8-10, ca. 50/50. Sample bottles were exposed to La Jolla, Calif., sunlight in June close to sea level for 2 weeks.

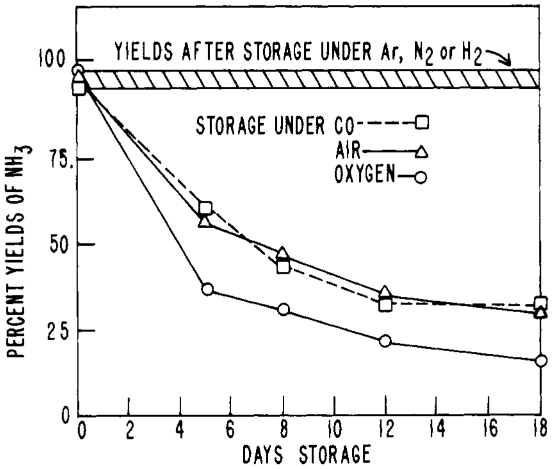

Figure 1. Dependence of the yields of ammonia on the storage history of a sample of TiO_2 doped with 0.1 wt % Fe_2O_3 (heated to 1000 °C in air for 1 h). Samples of this photocatalyst were stored under the respective gases at 1 atm of pressure. Nitrogen photoreduction experiments were performed after 5, 8, 12, and 18 days using 0.2-g samples in each case. The irradiation temperature was 50 °C, reaction time 2 h.

obtained at reaction temperature of 30 or 50 °C, respectively; lower irradiation temperatures could not be generated for technical reasons. Some N_2 is still photoreduced at 180 °C, however.

Gas Phase. The yields of NH_3 increase with increasing partial pressure of N_2 almost linearly in the range between 0 and 1.5 atm. Some NH_3 is formed upon illuminating H_2O-containing Fe-doped TiO_2 *in air* (see expt 23, Table II). A 1:1 N_2/H_2 mixture did not yield more NH_3 than the amount expected at the same partial pressure of N_2 in argon, indicating that the photosynthesis of NH_3 from the elements is not catalyzed (see expt 24, Table II).

Sample Storage History. The dependence of photocatalytic activity on the sample storage history introduces additional complexity into the present systems. If the samples of doped or undoped TiO_2 are stored under argon, N_2 or H_2, no substantial decline in photocatalytic efficiency is observed. Normal storage in air, oxygen, or CO causes a substantial loss of activity over a period of 2-3 weeks (Figure 1). This inactivation is attributed to the occupation of binding sites and micropores by O_2 or CO.

Heat Treatment. As was outlined above, heat treatment of the doped and undoped TiO_2 samples causes conversion from the anatase to the rutile modification, progressive loss of surface Ti-OH groups, and recrystallization of the rutile crystals formed; all factors contribute to the observed diminution of photocatalytic activity as the heating time is increased. Table III summarizes a number of pertinent experimental results which indicate that the photocatalysts lose activity after prolonged heat pretreatment.

Nitrogen Reduction in Sunlight. Table IV shows that the exposure of Fe-doped TiO_2 to normal sunlight is sufficient to bring about N_2 photoreduction. Illumination with a 500-W tungsten filament lamp emitting light at maximum intensities between 520 and 575 nm and tailing off toward the near-UV region did not produce measurable yields of NH_3. The Hg arc lamp employed in our other experiments produces sufficient radiation in the near-UV region (390-420 nm), corresponding to the absorption edge of TiO_2; the use of quartz instead of glass vessels had no effect on the yields.

Repeated Use of Photocatalyst and Ammonia Recovery. For potential practical application the repeated use of the titania photocatalysts seemed desirable and other methods than ex-

Table V. Effects of Metals on Nitrogen Photoreduction. Yields of NH_3 Determined after 3 h of UV Irradiation at 40 °C in Glass Vessels Containing 0.2 g of the Doped Titanias and N_2 at 1 Atm

No.	Metal[a]	Rutile/anatase	NH_3 yields, μmol
1	Fe	~95:5	6.4
2	Co	30:70	3.8
3	Mo	30:70	4.0
4	Ni	10:90	1.76
5	None	95:5[b]	1.35
6	Pd	~5:95	0.65
7	Pt	~5:95	0.43
8	Ag	~5:95	0.21
9	Au	~5:95	0.25
10	V	~5:95	0.25
11	Cr	~5:95	0.22
12	Pb	~5:95	0.19
13	Cu	~5:95	0.17

[a] Metal concentration 0.4 wt % in all cases. All samples were heated in air to 1000 °C for 2 h prior to rehumidification and irradiation except where indicated. [b] After 5 h of heating to 1000 °C.

Table VI. Effect of N_2 on the Photoreduction of C_2H_2 on Doped and Fe-Doped Incompletely Outgassed and Rehumidified TiO_2. Yields of Products Measured after 3 h of UV Irradiation

No.	Photo-catalyst[a]	Irradiation temp, °C	% C_2H_2 reduced[b] (Ar/N_2)	Yields (Ar/N_2), nmol CH_4	C_2H_4	C_2H_6	NH_3
1	TiO_2	40	0.025/0.005	12/10	15/2	0/0	0/0.37
2	TiO_2	120	0.080/0.020	35/10	30/10	0/0	0/0.32
3	TiO_2	180	0.44/0.28	50/27	10/8	2/1	0/0.14
4	TiO_2/0.2% Fe_2O_3	40	0.020/0.005	15/10	10/1	0/0	0/3.1
5	TiO_2/0.2% Fe_2O_3	120	0.084/0.060	55/40	35/25	15/5	0/0.35
6	TiO_2/0.2% Fe_2O_3	180	1.0/0.76	210/160	500/370	11/10	0/0.24

[a] Samples were pretreated by heating for 1 h at 1000 °C in air followed by storage in H_2O-saturated argon atmosphere. The TiO_2 consisted of a 10:90 mixture of rutile and anatase; the Fe-doped TiO_2 of 23:77% rutile and anatase, respectively. Sample size: 0.2 g in all experiments. [b] The partial pressures of Ar and N_2 were 1 atm at 25 °C. Initial concentration of C_2H_2 in gas phase: 85 μmol.

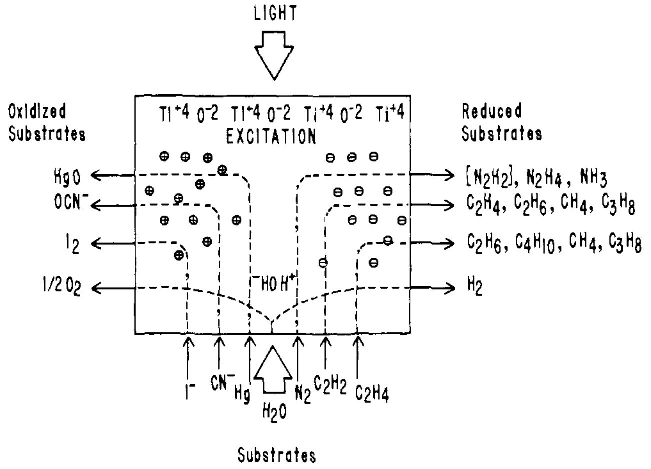

Figure 2. Schematic representation of photooxidation and -reduction reactions on incompletely outgassed rutile.

traction for NH_3 removal would have to be employed. No apparent loss of photocatalytic activity occurred when the TiO_2 samples were dried and outgassed at 250 °C in vacuo after extraction with H_2O and repeated UV irradiation. Approximately two-thirds of the NH_3 formed can be removed by vacuum degassing of the photocatalysts at about 250 °C.

Effects of Metal Dopants. In addition to iron a number of other metal dopants were tested in an effort to increase the photocatalytic activity of TiO_2. Enhanced yields of NH_3 as compared to those obtained with undoped TiO_2 were observed in samples containing Co, Mo, and Ni. These metals also caused partial conversion of anatase into rutile under the conditions of heat treatment chosen. Table V shows that a number of other metals did not produce active photocatalysts nor accelerated the anatase → rutile conversion.

Effect of N_2 on the TiO_2-Sensitized Photoreduction of C_2H_2. Although a study of the photoreduction of C_2H_2 was not within the scope of the present work, it became of interest to determine the effect of N_2 on the photoreduction of C_2H_2 at low partial pressures, i.e., under conditions where N_2 was expected to have the strongest inhibitory effect. Table VI reveals that C_2H_2 photoreduction under Ar at 40 °C produces CH_4 and C_2H_4 as the main products. At irradiation temperatures of 180 °C, the yields of these products increase and some C_2H_6 is also formed. Under the conditions chosen, N_2 had a significant inhibitory effect at low irradiation temperature and influenced mainly the C_2H_4 production. At higher irradiation temperatures the hydrocarbon product yields increase and the inhibitory effect of N_2 diminishes but is still clearly noticeable.

Discussion

The photolysis of H_2O and TiO_2 electrodes formally resembles the primary stage of photosynthesis and has received attention for possible applications in energy conversion technology:[6-8]

$$H_2O^l + nh\nu \xrightarrow{[TiO_2]_s} H_2{}^g + {}^1\!/_2O_2{}^g$$

$$\Delta G^{298} = 68.35 \text{ kcal/mol} \quad (1)$$

Our work indicates that molecular nitrogen has no effect on the yields of O_2 but inhibits the evolution of H_2 as compared to reaction eq 1 conducted under argon. Instead of H_2, NH_3 and traces of N_2H_4 are formed under N_2, in amounts consistent with the stoichiometry of reaction eq 2 and 3:

$$N_2{}^g + 3H_2O^l + mh\nu \xrightarrow{[TiO_2]_s} 2NH_3{}^g + 1.5O_2{}^g$$

$$\Delta G^{298} = 183 \text{ kcal/mol} \quad (2)$$

$$N_2{}^g + 2H_2O^l + xh\nu \xrightarrow{[TiO_2]_s} N_2H_4{}^l + O_2{}^g$$

$$\Delta G^{298} = 149.7 \text{ kcal/mol} \quad (3)$$

Reaction eq 2 and 3 are linked to the ability of TiO_2 to chemisorb both H_2O and N_2 and closely related to the photolysis of H_2O according to eq 1. The photolysis of H_2O on TiO_2 has been described[6-8] in line with current concepts of the electronic of semiconducting solids. Upon illumination with near-UV light electrons from the valence band are excited into the lowest conduction band; the band gap is in the order of 2.9–3.2 eV (390–420 nm),[11] corresponding to between 70 and 80 kcal, thus sufficient for reaction eq 1 to occur. The positive holes generated in the valence band provide the sites for oxygen production or other oxidation reactions. The electrons in the conduction band can be utilized for the reduction of substrates such as H^+, C_2H_2, C_2H_4, and, as we found, N_2. The overall processes are schematically represented in Figure 2. It is also possible, however, to describe the electrons in the conduction band as excited titanium atoms in lower oxidation states at which the reduction of the substrates occurs. N_2 and C_2H_2 both inhibit the H_2 evolution and thus may be assumed to be reduced at the same site or sites. Since H_2 is formed in reactions involving the transfer of two electrons and the production of C_2H_4 from C_2H_2 is inhibited by N_2 we assume that chemisorbed N_2 is reduced, at least in part, via chemisorbed diimide. Anatase, outgassed in vacuo at 200 °C, exhibited significantly lower photocatalytic reactivity than TiO_2 samples that were partially or completely converted into rutile. The anatase → rutile conversion is accelerated by iron oxides. Anatase doped with 0.2 wt % Fe_2O_3 may be converted into a conglomerate of Fe-doped rutile and anatase by heating to 1000 °C. Such doped TiO_2 samples have previously been shown to be strongly phototropic[10] and were found to be more active photocatalysts. Table V indicates that doping with oxides of cobalt, molybdenum, and nickel also increases the photocatalytic activity albeit not quite as strongly as Fe_2O_3. These metal oxides accelerate the anatase → rutile conversion. No enhancement of activity was observed on doping with eight other metals including Pd, Pt, Ag, Au, V, Cr, Pb, and Cu. Among this group the more noble metals are known to undergo *photoreduction,* giving rise to latent metallic images which disappear on exposure to oxygen.[12] The occurrence of such photoreduction processes may be responsible for the low activity of these metal-doped TiO_2 samples. Other factors which influence the photocatalytic activity of rutile are the active surface and the concentration of chemisorbed water or of surface Ti–OH groups. Prolonged thermal pretreatment causes the loss of chemisorbed H_2O and induces the growth of rutile crystals. After rehumidification these samples are photocatalytically less active than those heated for shorter periods; fine adjustment of the thermal pretreatment, outgassing, or rehumidification procedures is likely to produce photocatalysts with higher efficiency for possible use in nitrogen reducing solar cells. It remains to be seen if N_2 photoreduction also occurs on painted surfaces containing TiO_2 and if this reaction contributes to scaling or other adverse effects. Mechanistic aspects of this N_2 photoreduction are presently being investigated in conjunction with studies on the photocatalytic activity of other solids. Initial experimental results with α-Fe_2O_3 show that solids other than TiO_2 also catalyze N_2 photoreduction. The results with Fe_2O_3 are of interest as they suggest that the photoreduction of N_2 could have been possible under prebiotic conditions on earth. The photochemistry on Mars, whose atmosphere also contains some N_2, should be examined within this context.

Experimental Section

Reagents and Chemicals. Titanium dioxide of 99.9% purity (anatase) and a particle size of 2 μ was purchased from Alfa Products (Ventron) and was used without further purification excepting the heat treatment described below. Compressed gasses (Ar, N_2, and H_2) were 99.991% pure and used as such. Acetylene (Matheson) was passed through two gas-wash flasks filled with H_2O and stored in rubber serum capped glass bottles from which samples were withdrawn as needed and injected into the reaction vessels.

TiO_2 Sample Preparation. Except where indicated, the TiO_2 powder was heated to 1000 °C in air for 1-4 h. After cooling the samples were stored in Ar or N_2 filled desiccators containing H_2O instead of drying agent. The TiO_2 samples remained white after the thermal pretreatment, indicating the absence of any significant amounts of lower titanium oxides. Iron-doped TiO_2 was prepared by impregnating anatase with solutions of ferric sulfate. The resulting slurries were dried in rotating vacuum evaporators and subjected to the 1000 °C heat treatment in air as described above. TiO_2 samples doped with other metals were prepared analogously. Representative samples of the photocatalysts were examined by scanning electron microscopy; the composition was checked by elemental analyses.

Assays. Ammonia was determined colorimetrically by the method of Kruse and Mellon.[13] The light-exposed TiO_2 samples were suspended either in 1 N aqueous HCl or H_2O, the slurries were placed in centrifugation tubes, and the TiO_2 was removed by centrifugation. The extracts were made alkaline and subjected to distillation in a micro-Kjeldahl apparatus. The ammonia was determined in the distillates. In the experiment with $^{15}N_2$-enriched N_2, the H_2O extract was placed in one arm of a Rittenberg apparatus and the NH_3 and N_2H_4 were oxidized to N_2 with alkaline hypobromite, collected, and processed as outlined in ref 14. Hydrazine was determined in the centrifugated 1 N HCl extracts with *p*-dimethylaminobenzaldehyde.[15] The hydrazone was extracted into 5 mL of CH_2Cl_2 and the absorbance was measured at 458 nm.

Hydrogen and oxygen were determined by GLC using a column of 6 ft length filled with molecular sieve (5 A), at the operating temperature of 27 °C. Hydrocarbons (CH_4, C_2H_2, C_2H_4, etc.) were determined using a phenyl isocyanate-Porasil 80-100 mesh column.

Standard Experimental Technique. Unless indicated, all experiments were performed in glass flasks of 38 mL total capacity, manufactured by Pierce Chemical Co., Rockford, Ill. The titania powders were placed into the N_2- or Ar-filled flasks which were subsequently sealed with silicone rubber seals. As a rule, six irradiation experiments were performed simultaneously. For this, the bottles were fastened on a specially designed rack which was placed above a 360-W Hanovia mercury arc UV lamp at a distance of about 20 cm. A stream of cold air was blown through the irradiation chamber to maintain the "irradiation temperature" constant to within ±5 °C, as measured with a thermometer placed on the bottle rack. The irradiation time was 3 h in most experiments or as indicated. After termination of individual experiments, 10 mL of 1 N HCl was injected directly into the reaction flasks and the resulting suspensions were worked up as described above. In the experiments with C_2H_2 as the substrate, 2 ml of C_2H_2 at 1 atm of pressure was injected into the reaction flasks at $t = 0$. For product analysis, samples were withdrawn at convenient time points. The hydrocarbons were identified by measurements of the GLC retention times, coinjection of authentic compounds, and mass spectrometry.

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References and Notes

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