PhC≡CH, 536-74-3; 1,2-benzenediol, 120-80-9; hydrazobenzene, 122-66-7; hydroquinone, 123-31-9; ascorbic acid, 50-81-7.

Supplementary Material Available: Listing of atomic coordinates, thermal parameters, and molecular dimensions for **4** and **6** (15 pages). Ordering information is given on any current masthead page.

Photochemical H_2 Generation by Visible Light. Sensitization of TiO_2 Particles by Surface Complexation with 8-Hydroxyquinoline

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The surface modification of large band gap semiconductors such as TiO_2 and SnO_2 by adsorbed or covalently linked photoactive dyes is a subject of increasing investigation[1,2] in view of potential applications to solar energy conversion. In both photoelectrochemical cells[1] and H_2-generating photochemical systems,[2] the phenomenon of photosensitized charge injection is used to effect charge separation with light of less than band gap energy. We wish to report here our preliminary results concerning the surface modification of anatase TiO_2 by the prototype dye 8-hydroxyorthoquinoline (HOQ) and the ability of such modified TiO_2 powders to generate H_2 in a sacrificial water reduction system using visible light. Initial evidence for H_2 production via a charge injection mechanism will be presented.

When powdered TiO_2 is introduced into aqueous solutions of HOQ (solubility $\leq 4 \times 10^{-3}$ M), a bright yellow orange color develops on the powder while the supernatant absorption spectrum shows simply a decrease in free HOQ.[3] No pH change accompanies this process. We believe that the color change is due to the formation of surface Ti(IV)–OQ complexes, most likely through the so-called "esterification" of surface hydroxyl groups with concomitant loss of water. Such reactions between TiO_2 and other alcohols are well documented.[4] Our evidence for this reaction is twofold. First, color development in samples where HOQ is added to optically transparent TiO_2 colloid[5] is quite slow and is considerably slower in base than in acid. HOQ (10^{-4} M) adsorption onto 1 g/L TiO_2 is complete in 1 h at pH 2.5 and in 5 days at pH 12.8. Second, the spectrum of the HOQ-modified colloidal TiO_2 differs greatly from that of either free HOQ, OQ^-, or H_2OQ^+ (Figure 1). Both the position and intensity of the 380-nm absorption band are very similar to that observed for $M(OQ)_n$ complexes where M is a closed d-shell metal ion. This transition has been assigned as a ligand localized transition for all such complexes.[6,7]

Complexation between HOQ and anatase TiO_2 powder was compared for three powders, Degussa P-25 (surface area 55 m^2/g), Bayer "Bayersol" (surface area 180 m^2/g), and Montedison TiO_2-U, an anatase powder doped with 0.4% Nb and loaded with 0.2% RuO_2 by weight (surface area ~ 200 m^2/g). In saturated aqueous solutions of HOQ containing 1 g/L TiO_2, HOQ uptake was found to be 300 μequiv/g for Degussa P-25, 800 μequiv/g for Bayersol, and 1000 μequiv/g for TiO_2-U. These data are consistent with a previous report of 200 μequiv/g for uptake of HOQ by Degussa P-25 from benzene solution[3] and indicate that complexation is roughly proportional to surface area. Emission, typically an easily detectable property of HOQ and closed d-shell $M(OQ)_n$ complexes,[6,7] could not be detected from either solid samples of HOQ modified TiO_2 powder or modified colloidal TiO_2 at room temperature using a Perkin-Elmer MPF 44A spectrofluorimeter. Nanosecond flash photolysis[8] of HOQ-modified TiO_2 colloid showed no emission or transients, indicating that the excited state lifetime or the surface Ti(IV)–OQ complex is less than the 11–25 ns typically observed for emissive $M(OQ)_n$ complexes in DMF.[7] Exaustive photolysis of the same samples with ≥435-nm light resulted in no photodecomposition after 17 h.

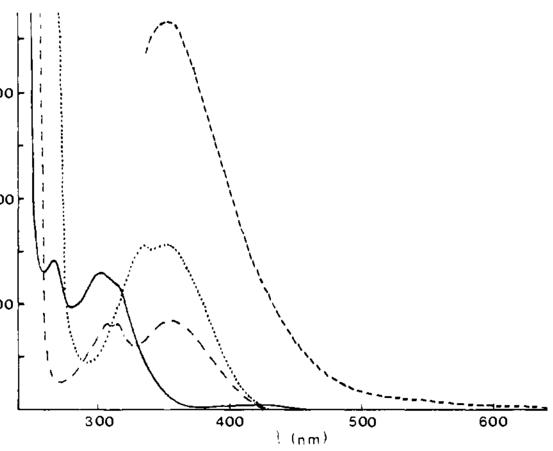

Figure 1. Optical absorption spectra of HOQ: (—) in neutral H_2O; (···) pH 10, (-·-·) pH 1.6, (- - -) on colloidal TiO_2 (1 g/L) at pH 2.5 (vs. colloidal TiO_2 reference).

Table I. Comparison of the Sensitizing Ability of HOQ and a Surfactant Ruthenium Bipyridyl Complex for Different Anatase TiO_2 Powders in a Sacrificial H_2-Generating System

	μL H_2/h[a]
HOQ on TiO_2	
Degussa P-25	300–420
Bayersol	800–1220
TiO_2-U	750–1000
TiO_2-U without Pt[b]	310–350
$Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$	
Degussa P-25	700–840
Bayersol	700–800
TiO_2-U without Pt[b]	800–1080

[a] In a 5-mL sample, 5-mL headspace. Range of values is the total obtained from 6–8 repeats. [b] H_2-generating catalyst in this case is 0.2% RuO_2 initially present on the TiO_2.

HOQ-modified TiO_2 powder proved to be an excellent photosensitizing agent in the following sacrificial water reduction system. Samples, 5 mL, were made up containing 10^{-3} M HOQ equilibrated with 5 mg of TiO_2 powder, 2×10^{-2} M EDTA as a sacrificial electron donor, and 10 mg/L Pt (0) sol.[9] For comparison, analogous samples were made up in which 10^{-4} M surfactant $Ru(bpy)_2(4,4'\text{-tridecyl-}2,2'\text{-bpy})^{2+}$ was physisorbed onto the TiO_2, and HOQ was omitted. At these concentrations, light absorption by the insoluble ruthenium complex is 2–6 times that of the HOQ-modified TiO_2, depending on the surface area of the TiO_2 used, and light absorption ≥435 nm by free HOQ is negligible.

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(1) (a) Giraudeau, A.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 5137–5142 and references therein. (b) Ghosh, P. K.; Spiro, T. G. *Ibid.* **1980**, *102*, 5543–5549 and references therein. (c) Dare-Edwards, M. P.; Goodenough, J. B.; Hamnet, A. J.; Seddon, K. R.; Wright, R. D. *Faraday Discuss. Chem. Soc.* **1980** *No. Disc. 70*, 285–298.

(2) Borgarello, E.; Kiwi, J.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Nature (London)* **1981**, *279*, 158–160.

(3) This phenomennon was first noted by: Boehm, H. P. *Faraday Discuss. Chem. Soc.* **1971**, *52*, 264–275.

(4) Parfitt, G. D. *Prog. Surf. Membr. Sci.* **1976**, *11*, 181–226.

(5) Moser, J.; Grätzel, M. *Helv. Chim. Acta* **1981**, *65*, 1436–1444. Preparation of the basic colloid: Moser, J., unpublished results.

(6) Lytle, F. E.; Storey, D. R.; Juricich, M. E. *Spectrochim. Acta* **1973**, *29A*, 1357–1369.

(7) Scandola, F.; Ballardini, R.; Indelli, M. T. In "Photochemical Photoelectrochemical, and Photobiological Processes"; Hall, D. O., Palz, W., Eds.; Reidel: Dorecht, 1982; p 66–75.

(8) Laser flash equipment is described in: Rothenburger, G.; Infelta, P.; Grätzel, M. *J. Phys. Chem.* **1981**, *85*, 1850–1856.

(9) See: Brugger, P. A.; Cuendet, P.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 2923–2927, for Pt preparation. Centrifugation and supernatant analysis confirmed that complete deposition of Pt onto the TiO_2 particles takes place. Platinization of TiO_2 by sol deposition prior to complexation by dye results in a system with slightly less activity but with similar stability.

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Samples were sealed in 10-mL gas-tight Wheaton serum vials, deoxygenated by argon bubbling, and irradiated ≥435 nm with a 450W Xe lamp in a stirred, thermostatted rotating sample holder described elsewhere.[10] After varying degrees of photolysis, samples were centrifuged, and the supernatant was analyzed spectrophotometrically for signs of loss of free HOQ.

The performance of the different modified TiO_2 powders can be seen in Table I. HOQ-modified TiO_2 samples compare favorably with surfactant ruthenium bipyridyl modified samples, despite lower light absorption. The quantum yield, ϕ_{H_2}, expressed as moles H_2 per mole of incident (not absorbed) photons was measured for HOQ-modified TiO_2-U samples prepared as described above, but without Pt. (The active H_2-generating catalyst in this case is provided by the 0.2% RuO_2.) The spatially dispersed lines of a Coherent Radiation argon ion laser were used to irradiate vigorously stirred samples at 457.9 and 514.5 nm at intensities of 100–200 mW. The actinometer used was $Co(en)_2(SCH_2CH_2NH_2)^{2+}$ at pH 2.[11] ϕ_{H_2} was found to be 0.0034 at 457.9 nm and 0.0014 at 514.5 nm for HOQ-modified TiO_2-U. No correction was made for significant light losses due to scattering from the optically opaque suspensions, or for incomplete light absorption by the surface Ti(IV)–OQ complex. Rough correction for the expected difference in absorption by the complex at 457.9 and 514.5 nm suggests that ϕ_{H_2} is essentially the same at both wavelengths. These numbers can be compared with the value $\phi_{H_2} = 0.007$ obtained by Miller and McLendon[12] for the well-studied sacrificial system $Ru(bpy)_3^{2+}/MV^{2+}$/Pt sol/EDTA at pH 5 under conditions of essentially total light absorption. From the data in Table I, it is clear that the addition of Pt catalyst will significantly improve ϕ_{H_2} for HOQ-modified TiO_2.

Initial rates of H_2 production could be sustained for over 15 h (>40 turnovers with respect to HOQ) in samples where EDTA was replenished before the concentration dropped below 15 mM and where H_2 was regularly removed by argon purging. No loss of supernatant HOQ was observed. In samples photolyzed to extensive EDTA depletion, loss of supernatant HOQ was observed after ca. 25% loss of EDTA (assuming 2 equiv/mol); however, no drop in the rate of H_2 production was seen. Trivial blank photolysis experiments in which either HOQ or TiO_2 were omitted gave no H_2 due to the lack of light absorption. Ti(IV)–OQ complexes synthesized in nonaqueous solvents could not be used to investigate the role of bulk TiO_2 in the H_2-generating mechanism, as aqueous hydrolysis resulted in the immediate formation of TiO_2 precipitate. However, HOQ was found to form an analogous bright yellow complex with neutral Al_2O_3 chromatographic powder,[12] but this powder proved to be completely inactive when substituted for HOQ-modified TiO_2 in the H_2-generating system. This suggests that the semiconductor properties of the TiO_2 particle are involved in the function of the HOQ-modified TiO_2 in this system.

The mechanism for H_2 generation most consistent with the chemical and photophysical data presented above is one of excitation of surface Ti(IV)–OQ species, followed by charge injection into the TiO_2 particle bulk. EDTA serves to rereduce the oxidized surface species before decomposition occurs,[13] while the electron is channeled to a Pt or RuO_2 catalyst deposit on the particle where reduction of H^+ takes place. We have found preliminary evidence for photosensitized charge injection in photoelectrochemical cells containing HOQ-modified polycrystalline TiO_2 electrodes[14] and are presently pursuing this investigation in depth. The extention of this work to other dye analogues capable of absorbing more of the solar spectrum is an obvious one, and as such, HOQ-modified TiO_2 represents a prototype system of great importance in the field of photochemical conversion research.

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Registry No. 8-Hydroxyquinoline, 148-24-3; anatase, 1317-70-0; platinum, 7440-06-4; ruthenium dioxide, 12036-10-1; hydrogen, 1333-74-0; water, 7732-18-5; EDTA, 60-00-4.

Supplementary Material Available: Graph of photocurrent from HOQ-modified polycrystalline TiO_2 electrode (1 page). Ordering information is given on any current masthead page.

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(10) Houlding, V. H.; Geiger, T.; Kölle, U.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1982**, 681–683. Because the samples are rotated through the light path, the incident light is less than for direct irradiation.

(11) Houlding, V. H.; Mäcke, H.; Adamson, A. W. *Inorg. Chem.* **1981**, 20, 4279–4285.

(12) Baker alumina (stock no. 0537) was used (surface area 220 m^2/g by BET), and approximately 1 mequiv/g HOQ was adsorbed onto the surface. This does not correspond to saturation of the surface. Pt sol was deposited in a manner analogous to the TiO_2 samples, and centrifugation revealed no residual Pt in solution.

(13) Cyclic voltammetric studies of HOQ at pH 7.0 (conditions: 1 mM HOQ, 0.2 M KCl, phosphate buffer, basal plane graphite electrode vs. Ag/AgCl, scan rate 0.1 V/s) showed that both one-electron oxidation and reduction gave species that were chemically unstable. On the first anodic scan, oxidation occurred with E_{pa} 0.48 V, and the rereduction peak was minimal. The first cathodic scan showed a reduction at E_{pc} −1.1 V with no corresponding reoxidation wave. Subsequent scans were seriously distorted with respect to first scans. See also: Claret, J.; Muller, C.; Feliu, J. M.; Virgili, J. *Electrochim. Acta* **1982**, *27*, 1475–1479.

(14) Desilvestro, J.; Houlding, V. H.; Grätzel, M., to be published.

Carbon Monoxide Activation by Organoactinides. η^2-Acyl–CO Coupling and the Formation of Metal-Bound Ketenes

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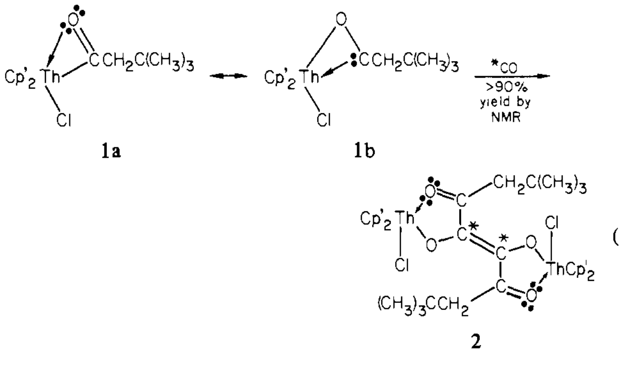
The coupling of metal carbenes (and carbynes) with CO to yield coordinated ketenes is a well-documented process.[1] We recently reported that the thorium acyl complex $Cp'_2Th[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ (**1**, $Cp' = \eta^5\text{-}(CH_3)_5C_5$) reacts with CO to yield the unusual dionediolate **2** (eq 1).[2] On the basis of ^{13}C labeling



1a **1b** **2** (1)

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(1) (a) Brown, T. J. *Prog. Inorg. Chem.* **1980**, *27*, 1–122 and references therein. (b) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. (c) Miyashita, A.; Grubbs, R. H. *Tetrahedron Lett.* **1981**, 1255–1256. (d) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133–3135. (e) Herrmann, W. A.; Plank, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 525–526. (f) Redhouse, A. D.; Herrmann, W. A. *Ibid.* **1976**, *15*, 615–616. (g) Kreissl, F. R.; Eberl, K.; Nedelhoven, W. *Chem. Ber.* **1977**, *110*, 3782–3791. (h) Dorrer, B.; Fischer, E. O. *Ibid.* **1974**, *107*, 2683–2690.