Communications to the Editor

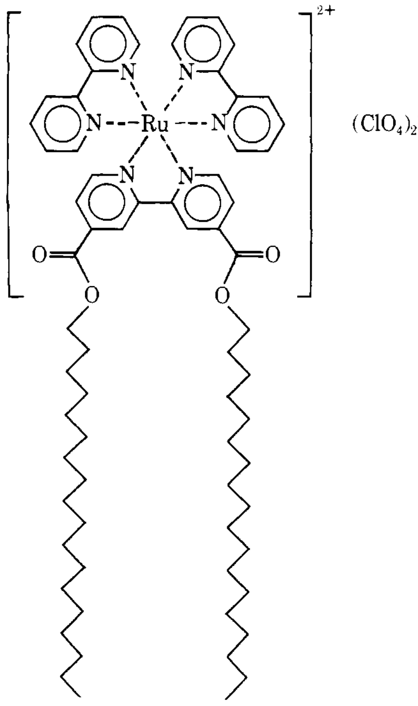
Photochemical Cleavage of Water: A System for Solar Energy Conversion Using Monolayer-Bound Transition Metal Complexes[1]

Sir:

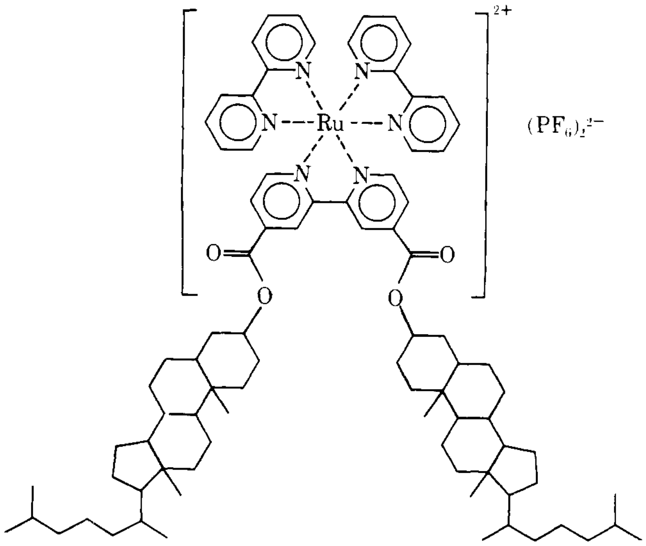
The search for new fuels, new sources of energy, and new methods for solar energy conversion is currently one of the most active areas of applied research. A frequently suggested route for solar energy conversion involves the photochemical conversion of readily available stable starting materials to high energy products. One of the most efficient processes for conversion of light energy into chemical energy has been shown to be photoinduced electron transfer. It has recently been shown that excited states of transition metal complexes such as tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ (**1**) can serve as both electron acceptors and electron donors.[2-5] It has been demonstrated that, as an electron donor, essentially all the excitation energy of the complex can be utilized to transfer an electron to a long lived reduced species.[6] Although these reactions occur rapidly and efficiently in solution, their use as effective energy conversion processes is generally prevented by rapid return of the products to the unexcited starting materials in a succeeding electron-transfer event. A consideration of reduction potentials indicates that excited states of complexes such as **1** should be able to reduce water as hydrogen ion to hydrogen gas over a wide pH range; the fact that excited states of these complexes are not generally quenched by water or acid in solution suggests that barriers for the electron transfer process render it too slow to compete with excited state decay. Although photoinduced cleavage of water should be an attractive source of H_2 fuel, apparently the only successful use of light in this process has been in the "photoassisted" electrolysis of water at a titanium dioxide electrode.[7-9] In this communication we report a study of the photochemistry of a system consisting of surfactant derivatives of **1** incorporated into monolayer assemblies in contact with liquid water. Upon irradiation of this system with light absorbed by the ruthenium(II) complex, cleavage of water to yield hydrogen and oxygen occurs.

Surfactant analogues of **1**, **2a**, and **2b** were prepared by replacing a single 2,2′-bipyridine unit with the dioctadecyl or bis(dihydrocholesteryl) esters, respectively, of 4,4′-dicarboxy-2,2′-bipyridine.[10] In contrast to **1**, which is water soluble, **2a** and **2b** are completely water insoluble and form monolayer films when dilute chloroform solutions are spread on a water-air interface. The films from **2a** give good surface pressure-area isotherms for both the pure compound and for mixtures of **2a** with arachidic acid; an area of ca. 40 Å^2/molecule of **2a** is obtained for both pure and mixed layers at a pressure of 30 dyn/cm.[11] Monolayer assemblies containing an outermost hydrophobic layer of **2a** or **2b** could be obtained by transferring monolayer films of the complexes to glass slides or glass slides coated with a hydrophilic outer layer of arachidic acid using the usual monolayer assembling techniques.[12]

Absorption and emission spectra of **2a** incorporated into the assemblies described above are similar to those obtained for solutions of **1** and **2a**; the monolayer bound complex has absorption maxima at 377 and 430 nm with a tail to ca. 520 nm. The luminescence maximum is 660 nm with an estimated quantum efficiency of ca. 0.3 for freshly prepared layers,[11] close to the value of 0.27 reported for solutions of **1** in EPA.[13] The luminescence from monolayer assemblies containing an outer layer of **2a** is almost *entirely quenched* upon immersion of the assembly into water. Quenching is observed for both degassed and undegassed water. In contrast, no quenching of the solution luminescence is observed when up to 25% of water, concentrated (38%) HCl, acetic acid, or 2% NaOH solutions are added to dioxane solutions of **2a**. No changes in the absorption spectrum of **2a** are observed after the assemblies are treated with water in the dark or under irradiation. The luminescence from assem-



2a



2b

blies containing **2a** can be regenerated by gentle heating under vacuum.

When glass slides containing monolayer assemblies of **2a** or **2b** are immersed in water and irradiated through Pyrex with a 100-W medium-pressure mercury lamp, a steady production of gas is observed. In a typical experiment irradiation of a set of ten slides containing a single outer monolayer of **2a** led to the production of 0.5 cm^3 of gas ($\sim$1 atm of pressure) during a 24-h period. (The average absorption per slide in the visible-near uv region was 0.1-1%). The **2a** used in the gas generation is evidently almost completely recyclable since an estimated turnover of more than 10^3 molecules of gas/molecule of **2a** has been observed in a system now in its second week of operation. Analysis of the gas in a mass spectrometer indicated that it contained molecular hydrogen and oxygen;[14] this was confirmed by an experiment in which the collected gas was found to undergo explosive combustion upon ignition.

The reasonable conclusion from the above results is that the net reaction observed is given by eq 1-2.[14]

$$2a \xrightarrow{h\nu} 2a^* \qquad (1)$$

$$2(2a^*) + H_2O \rightarrow H_2 + \tfrac{1}{2}O_2 + 2(2a) \qquad (2)$$

The reaction is reasonable on energetic grounds since the 45-40 kcal/mol excited state of **2a** has more than enough energy to promote the separation of water (28 kcal/mol of electrons). The ruthenium(III) complex produced by oxidation of **2a*** should be able to oxidize OH^-; in fact, it has recently been shown[15] that oxidized **1** reacts with OH^- to generate O_2. The fact that similar ruthenium(II) complexes are reactive in monolayer assemblies but not in solution is evidently due to a lowering of the barrier to the electron transfer process in the assembly or to provision in the assembly of a barrier to the geminate recombination with the ruthenium site since the lifetime of the excited state of the complex in the dry assembly and in solution are not very different. It seems likely that the hydrophobic environment provided by the assemblies assists in establishing these barrier conditions although a detailed mechanism cannot yet be established.

The results presented here represent a novel method for preparation of hydrogen and oxygen that appears extremely promising as a means of solar energy conversion. Experiments are currently in progress to determine the scope, efficiency, and mechanism of this process.[16]

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References and Notes

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(10) Synthetic details will be reported in the full paper.

(11) We thank Dr. D. Möbius at the Max Planck Institute in Göttingen, Germany for making these measurements.

(12) H. Kuhn, D. Möbius, and H. Bücher, "Physical Methods of Chemistry", Vol. I, Part 3B, A. Weissburger and B. Rossiter, Ed., Wiley, New York, N.Y., 1972, p. 588.

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(14) Although both mass spectral analysis and combustion clearly establish the production of hydrogen, the determination of oxygen as the major oxidative product is less certain since a background from oxygen in the air was unavoidably present. However, this point is not critical since it has been shown that ruthenium(III) complexes liberate O_2 from OH^-.[15] Note Added in Proof. Recent experiments have established that oxygen is the major oxidative product of water in these reactions; in some cases the hydrogen/oxygen ratio appears to be lower than that predicted by eq 2. This may be due to trapping of the hydrogen precursor by unsaturated groups in the monolayer.

(15) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2858 (1975).

(16) The quantum yield can be very approximately estimated to be ca. 0.1 when pure water is used as the substrate. The reaction appears to be somewhat pH dependent with a slight retardation at high pH.

Gerhard Sprintschnik, Hertha W. Sprintschnik
Pierre P. Kirsch, David G. Whitten*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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Binuclear Nature of the Aquomolybdenum(IV) Ion in Solution

Sir:

In a recent communication[1] Sykes and co-workers rejected the binuclear structure $Mo_2O_2^{4+}$ assigned to the molybdenum(IV) aquo ion by Ardon and Pernick,[2] and support the mononuclear structure[3] MoO^{2+} (or $Mo(OH)_2^{2+}$). The purpose of the present communication is to show why a mononuclear structure of Mo(IV) is unacceptable and to report new data that confirm the binuclear structure of this ion.

In 1966, Souchay[3] and co-workers discovered the existence of Mo(IV) as a stable species in aqueous solution. Unfortunately, this important discovery was totally overlooked by the numerous reviews and textbooks dealing with molybdenum chemistry that were published in the U.S.A. and U.K. between 1966 and 1973, all of which upheld the wrong notion that Mo(IV) could *not* exist as a stable species because of a supposed disproportionation reaction. These unusual circumstances explain, though by no means justify, Ardon and Pernick's unawareness of Souchay's work when they reported their own findings.[2]

The charge of a metal ion cannot usually be determined solely by its ion-exchange elution behavior, but a definite distinction may be made between a 2+ and 4+ charge of a transition metal ion by comparing its elution behavior with that of related ions of known charges.[4] The binuclear structure $Mo_2O_2^{4+}$ was assigned to the Mo(IV) aquo ion[2] on the basis of a charge per atom determination (2.0 ± 0.1) and the elution behavior which corresponded to that of other tetrapositive ions, but was in marked contrast to the elution behavior of dipositive transition metal aquo ions (including dipositive oxo ions). Further evidence of the binuclear structure is now presented.

The degree of polymerization of transition metal ions and other species which are stable only in acidic solutions may be determined directly by *acid cryoscopy*.[5]

Eutectic aqueous perchloric acid was the first solvent to be employed successfully for this purpose[6] and enabled the confirmation of the binuclear structure of the chromic dimer[6a] and of the Mo(V) aquo ion.[7] This solvent, however, could not be employed for the determination of the degree of polymerization of Mo(IV) since it is reduced by it to Cl^-. A second solvent, eutectic aqueous trifluoroacetic acid, was found to be suitable for cryoscopic work[8] and is not reduced by Mo(IV) or any other transition metal ion. At the concentration of 5.1 M this solvent has a eutectic freezing point of −22.465 ± 0.005 °C. The cryoscopic constant derived from