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Applications of Light-Induced Electron-Transfer and Hydrogen-Abstraction Processes: Photoelectrochemical Production of Hydrogen from Reducing Radicals

Sir:

Several recent studies have focused on the interception of long-lived or transient one-electron oxidants or reductants formed in light-induced electron-transfer processes. A number of heterogeneous or colloidal catalyst systems have been found useful for the coupling of multielectron redox reactions with reactions of the "one-electron" reagents to mediate the oxidation and/or reduction of water to oxygen and hydrogen.[1-9] Other investigations have demonstrated the possibility for obtaining a similar coupling of redox reactions through the use of photoelectrochemical cells.[10,11] In one study, it was found possible to couple the reduction of photogenerated $Ru(bpy)_3^{3+}$ in one cell with oxidation of Fe^{2+} in a second nonilluminated compartment.[10] More recently, it has been shown that hydrogen generation from a nonilluminated compartment containing aqueous acid can be coupled with oxidation of the methylviologen radical cation, MV^+, formed by irradiation of a compartment containing $Ru(bpy)_3^{2+}$, MV^{2+}, and triethanolamine.[11] In the present paper, we report a study of several photoprocesses which generate reducing radicals in similar photoelectrochemical cells. We find that coupling of a light-induced reaction to produce a photocurrent concurrent with hydrogen generation in a second compartment can occur for a number of electron transfers and hydrogen abstractions in what appears to be a fairly general process.

Photoelectrochemical cells used in these studies consisted of the following components: a nonirradiated cathode compartment equipped with platinum gauze (2 × 1 cm) or platinized platinum foil (4 × 1 cm) electrodes and filled with 1 M HCl, a photoanode compartment equipped with similar electrodes and filled with various stirred aqueous or nonaqueous solutions (see Table I), and a salt bridge consisting of 5 M KCl and agar for the aqueous system and 2 M tetraethylammonium perchlorate in pyridine–silica gel for the nonaqueous systems. Both compartments were deoxygenated by flushing with oxygen-free nitrogen for ca. 20 min. The photoanode compartment was irradiated with various wavelengths selected by a monochromator from a 1000-W mercury–xenon lamp. The current was measured with a microammeter and recorder; the gas produced in the cathode compartment was analyzed by gas chromatography.[12]

Table I. Substrate–Quencher Combinations Used in the Photoanode Compartment

substrate	quencher (M)	λ, nm	photocurrent, μA	efficiency, %[d]
benzophenone	2-propanol (6.5)	366	25	1.7
benzophenone	2-propanol (6.5)[a]	366	320	22.2
benzil	2-propanol (6.5)[a]	366	35	2.5
$TPP{\cdot}SnCl_2$	diisopropylethylamine (0.6)[b]	420	35	n.d.
RuL_3^{2+}	triethylamine (0.08)[b]	436	70	5.0
$RuL_3^{2+\prime}$	triethylamine (0.08)[b]	436	12	n.d.

[a] With 10 mmol of MV^{2+}. [b] In acetonitrile; 2 M Et_4NClO_4 in pyridine/silica gel used as salt bridge. [c] L′ = 5,5′-carboxy-2,2′-bipyridine diethyl ester. [d] Observed quantum yield for the electron flow under the experimental conditions described. The concentrations of the substrates are adjusted so that they absorb more than 99% of the light at the irradiation wavelength. Efficiencies are not corrected for the unquenched excited states.

Initial experiments employed the complex RuL_3^{2+}, where L = 4,4′-dicarboxy-2,2′-bipyridinediisopropyl ester, as the light-absorbing substrate together with triethylamine (0.08 M) in acetonitrile. Previous studies have indicated that quenching by electron transfer occurs on irradiation in a sequence indicated by eq 1 and 2.[13-15] Both of the radicals formed in the photolysis are good reductants, having potentials $E_{red/ox} \simeq$ 0.8–1.0 V.[14] Irradiation of this system in the presence of platinum catalysts and water has been found to lead to fairly efficient hydrogen generation.[12] Consequently, it was not surprising to observe that

$$RuL_3^{2+*} + Et_3N: \rightarrow RuL_3^{+} + Et_3N^{+\cdot} \tag{1}$$

$$Et_3N^{+\cdot} + Et_3N: \rightarrow Et_3NH^{+} + CH_3\dot{C}HNEt_2 \tag{2}$$

irradiation of the RuL_3^{2+}/Et_3N: photoanode compartment leads to production of a photocurrent (Table I) together with generation of hydrogen at the cathode. The photocurrent observed is a linear function of the square of the absorbed light intensity, indicating that both radicals generated in eq 1 and 2 are reactive in the electrode process, or alternatively that production of a second molecule of RuL_3^+ can occur via reaction 3. The quantum

$$RuL_3^{2+} + CH_3\dot{C}HNEt_2 \rightarrow RuL_3^{+} + CH_3CH{=}NEt_2^{+} \tag{3}$$

efficiency of the cell in terms of current produced per photon absorbed in this case is 5%, which is comparable to that obtained in other systems involving photoelectrochemical cells.[10,11] Similar results were obtained with other systems previously found to undergo reductive electron-transfer quenching by amines; lower photocurrents were obtained with tetraphenylporphyrintin(IV), and reversible spectral changes occurring during the photolysis suggested a buildup of the tin porphyrin radical.

A rather different type of reaction that also results in formation of two reducing radicals as primary photoproducts is the photoreduction of ketones and N-heteroaromatics by alcohols and other hydrogen atom donors. Irradiation of benzophenone in 2-propanol, for example, gives rise to potentially reducing ketyl radicals as indicated by eq 4.[16-18] Irradiation of benzophenone in partially

$$(C_6H_5)_2C{=}O^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2\dot{C}{-}OH + (CH_3)_2\dot{C}{-}OH \tag{4}$$

aqueous 2-propanol in the photoanode compartment of the cell

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(1) Lehn, J.-M.; Sauvage, J.-P. *Nouv. J. Chim.* **1977**, *1*, 449.

(2) Koryakin, B. V.; Dzabiev, T. S.; Shilov, A. E. *Dokl. Akad. Nauk SSSR* **1976**, *229*, 614.

(3) Koryakin, B. V.; Dzabiev, T. S.; Shilov, A. E. *Dokl. Akad. Nauk SSSR* **1977**, *238*, 620.

(4) Krasna, A. I. *Photochem. Photobiol.* **1979** *29*, 267.

(5) Moradpour, A.; Amouyal, E.; Keller, P.; Kagan, H. *Nouv. J. Chim.* **1978**, *2*, 547.

(6) Kalyanasundarum, K.; Kiwi, J.; Grätzel, M. *Helv. Chim. Acta* **1978**, *61*, 2720.

(7) Kiwi, J.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 860.

(8) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423.

(9) Kalyanasundarum, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 701.

(10) Durham, B.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6286.

(11) Durham, B.; Dressick, W. J.; Meyer, T. J. *J. Chem. Soc., Chem. Commun.* **1979**, 381.

(12) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4007.

(13) DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Meyer, T. J.; Whitten, D. G. *Adv. Chem. Ser.* **1978**, *No. 168*, 28.

(14) DeLaive, P. J.; Lee, J. T.; Sprintschnik, H. W.; Abruna, H.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 7094.

(15) DeLaive, P. J.; Foreman, T. K.; Giannotti, C.; Whitten, D. G., submitted for publication.

(16) For reviews, see: Scaiano, J. *J. Photochem.* **1973**, *2*, 81. Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.

(17) Gratzel and co-workers have observed that ketyl radicals can be scavenged by platinum catalysts to yield hydrogen directly.[18] We thank Professor Graatzel for a preprint of this work.

(18) Gratzel, C. K.; Gratzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7741.

0002-7863/80/1502-5119$01.00/0

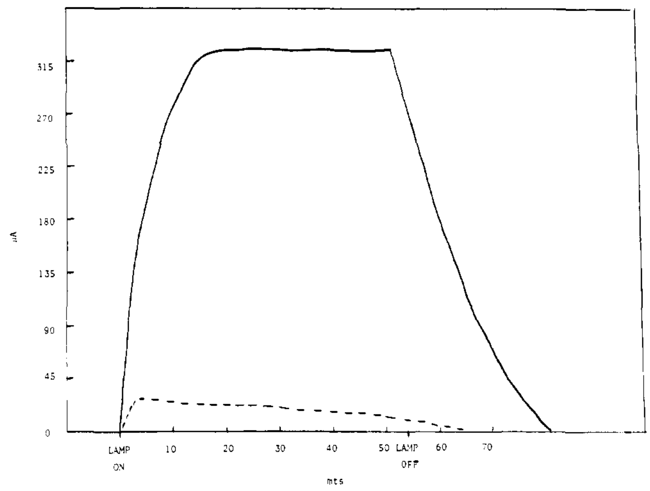

Figure 1. Plot of photocurrent with time for benzophenone/2-propanol/MV^+ in the photoanode compartment. Solid line: current in the presence of MV^{2+}. Dashed line: current in the absence of MV^{2+}. Abscissa is photocurrent in μA; ordinate is time in minutes.

described above does produce a small photocurrent; however, formation of the "normal" photoproduct, benzpinacol, is not entirely suppressed, indicating that oxidation of the ketyl radicals at the electrode is relatively inefficient compared to other processes. A striking increase in the efficiency of the photocurrent generated can be obtained by adding a small amount of methylviologen as a "mediator". MV^{2+} does not quench the benzophenone triplet efficiently, and under the reaction conditions, the quenching by MV^{2+} is negligible.[19] However, it is expected that MV^{2+} should efficiently oxidize both ketyl radicals as indicated in eq 5.[20] The

$$(C_6H_5)_2\dot{C}OH + MV^{2+} \rightarrow (C_6H_5)_2CO + H^+ + MV^+$$

$$(CH_3)_2\dot{C}OH + MV^2 \rightarrow (CH_3)_2CO + H^+ + MV^+ \qquad (5)$$

2-hydroxy-2-propyl radical reacts with the substrate, MV^{2+} in this case, rather than transferring hydrogen to Ph_2CO to yield another Ph_2COH radical.[21] Further, other studies have indicated that MV^{2+} can oxidize radical and diradical species generated in intra- and intermolecular hydrogen atom abstraction processes concurrent with transient or permanent formation of MV^+.[22-24]

In the present studies, irradiation of benzophenone/2-propanol/MV^{2+} solutions in the photoanode compartment (366-nm absorbed light, intensity 1.4×10^{-8} einstein/s) leads to a buildup of moderate levels of MV^+ and to a steady photocurrent of 320 μA (Figure 1). The $MV^{+\cdot}$ is oxidized at the anode of the photolyzed compartment with concomitant reduction of H^+ in the cathode compartment (1 M HCl). The two half-cell reactions are

$$\text{anode} \qquad MV^+ \rightarrow MV^{2+} + e^-$$

$$\text{cathode} \qquad h^+ + e^- \rightarrow {}^1/{}_2H_2 \qquad (6)$$

There was no decrease in benzophenone concentration over moderate periods of irradiation, and a steady production of hydrogen in the cathode compartment was observed. No benzpinacol could be detected for irradiation times on the order of 1-2 h. In these experiments as with the RuL_3^{2+}/Et_3N system, the photocurrent produced was linear with the square of absorbed light intensity. The quantum efficiency at the above-indicated intensity is 22%; quantitative analysis of the hydrogen produced gives good agreement with this value.

The overall reaction mediated by MV^{2+} in the photoelectrochemical cell is the oxidation of 2-propanol (eq 7). This reaction

$$(CH_3)_2CH{-}OH \rightarrow (CH_3)_2C{=}O + H_2 \qquad (7)$$

is endothermic by 20 kcal/mol so that as carried out the reaction involves simultaneous generation of electricity and chemical conversion. Given the wide variety of photoinduced electron-transfer and hydrogen atom abstraction processes previously reported, it should be possible to greatly extend the scope of these studies. For example, since both ketones and N-heteroaromatics can abstract hydrogen atoms from alkanes, it should be possible to mediate net dehydrogenation of alkanes, a process endothermic by ca. 33 kcal. Although the present studies with benzophenone require excitation in the near-UV, preliminary studies with benzil and acridine indicate modest photocurrents can be obtained with these systems by using longer wavelength light. We are currently extending our studies to systems in which other reducing species or potential oxidants can be generated by excitation in the visible region.

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[19] We measure $k_q = 1.03 \times 10^7$ M^{-1} s^{-1} for quenching of the benzophenone triplet by MV^{2+} under these conditions (quenching of phosphorescence in degassed acetonitrile). Therefore, only about 1.3% of the triplets is quenched by MV^{2+} whereas the remainder reacts with 2-propanol.

[20] Hyde, P.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1768.

[21] Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cummings Publishing Co.: CA, 1978.

[22] Small, R. D.; Scaiano, J. C. *J. Photochem.* **1973**, *6*, 543.

[23] Small, R. D., Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 828, 2126.

[24] Small, R. D., Scaiano, J. C. *J. Phys. Chem.* **1978**, *82*, 2662.

Propargylsilane and (Trimethylsilyl)alkyne Terminator Groups. Formation of an Exocyclic Allene in the Acetolysis of 8-(Trimethylsilyl)-6-octyn-2-yl Tosylate

Sir:

Triple-bond participation in reactions giving 6- and/or 5-membered rings was reported from our laboratories in 1966[1a] and 1969.[1b] Other related work appeared at approximately the same time.[2] More complex syntheses based on triple-bond cyclization have appeared.[3] Johnson and co-workers utilized the propyne terminator in their spectacular olefinic-acetylenic cyclizations to give steroidlike products.[4] For several reasons,[4d] still better terminators are needed, and the search for them is being actively pursued.[4]

We have now studied the cyclization in acetic acid of the tosylate **1** containing the previously uninvestigated propargylsilane terminator and, for comparison, the cyclization of tosylate **5** in which a terminally silylated alkyne, recently used also by others,[5,6] serves as the participating group (see Schemes I and II). The trimethylsilyl group present in **1** was expected to direct the cyclization toward 5-membered ring formation by β stabilization of the cationic transition state or intermediate **2**, which could lead to allene **4** or to cyclic vinylic acetates and products derived from them. The allylsilane group has played a comparable role in cyclizations reported in the literature,[7] including a steroid-forming

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[1] (a) Peterson, P. E.; Kamat, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3152. (b) *Ibid.* **1969**, *91*, 4521.

[2] (a) Clossen, W. D.; Roman, S. A. *Tetrahedron Lett.* **1966**, 6015. (b) Hanack, M.; Haffner, J.; Heterich, I. *Ibid.* **1965**, 875.

[3] Kozar, L. G.; Clark, R. D.; Heathcock, C. *J. Org. Chem.* **1977**, *42*, 1386.

[4] (a) Johnson, W. S.; Gravestock, M. B.; McCarry, B. E. *J. Am. Chem. Soc.* **1971**, *93*, 4332. (b) For a review see: Johnson, W. S. *Bioorg. Chem.* **1976**, *51*, 5. (c) For recent references and a report of a terminator containing an internal nucleophile, see: Garst, M. E.; Cheung, Y.; Johnson, W. S. *J. Am. Chem. Soc.* **1979**, *101*, 4404. (d) For a reevaluation of alkyne and alkene terminators, see: Johnson, W. S.; Hughes, L. R.; Carlson, J. L. *Ibid.* **1979**, *101*, 1281.

[5] Johnson, W. S.; Yarnell, T. M.; Meyers, R. F.; Morton, D. R. *Tetrahedron Lett.* **1978**, 2549.

[6] Brinkmeyer, R. S. *Tetrahedron Lett.* **1979**, 207.

0002-7863/80/1502-5120$01.00/0