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Photoelectrochemical Cells Based on Hydrogen-Atom Abstraction and Electron-Transfer Reactions in Solution: Systems Based on Benzophenone, 2-Propanol, Trialkylamines, and Methyl Viologen[†,2]

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Abstract: This paper reports the linking of well-studied solution photoprocesses such as hydrogen-atom abstraction by triplet benzophenone from 2-propanol and electron transfer from triethylamine to triplet benzophenone to proton reduction in aqueous acid via a two-compartment photoelectrochemical cell. In each case the intermediate reduction of *N,N'*-dimethyl-4,4'-bipyridinium (methyl viologen, MV^{2+}) provides a means for circumventing undesirable radical reactions and generating a stable carrier in high overall efficiency. The net result is reasonably efficient generation of a photocurrent concurrent with the occurrence of an endothermic reaction providing products that can in principle be recycled. An interesting aspect of this work is the finding that the overall efficiency of these cells is enhanced by the photochemical self-sensitization of MV$^+$ in the presence of 2-propanol or triethylamine and MV^{2+}.

Photochemistry is replete with reactions in which quenching of an excited state by atom or electron transfer efficiently generates ground-state products, one or both of which is a strongly oxidizing or reducing species. One of the most widely and thoroughly studied of such reactions is the photoreduction of ketones by alcohols.[3-8] This reaction was very early suggested to involve generation and subsequent reaction of what are now recognized to be strongly reducing ketyl radicals.[3] That the reaction clearly proceeds via the n,π^* triplet state in the case of benzophenone reduction was demonstrated by the elegant pioneering work of Hammond and his co-workers;[4-6] their studies together with those of Bäckstrom[8] and Pitts[7] clearly demonstrated that these reactions involve highly efficient generation of ketyl radicals via hydrogen-atom transfer and their subsequent disappearance via pinacol formation and secondary H-atom-transfer processes leading to net reduction or disproportionation back to starting materials. Subsequent investigations have established that ketyl radicals can be generated from excited states of benzophenone and other ketones by a sequence of electron transfer followed by proton transfer.[9-12]

One of the major goals of many current photochemical investigations is the efficient utilization of reactive species such as ketyl radicals or other one-electron oxidants or reductants to accomplish useful net chemical conversion. The relatively strong reducing power of ketyl radicals has been demonstrated in a number of investigations. For example, several studies have shown that oxidants such as methyl viologen (MV^{2+}) (*N,N'*-dimethyl-4,4'-bipyridinium) are efficiently reduced by ketyl radicals.[13-15] A more recent study has demonstrated that colloidal platinum can intercept ketyl radicals generated by irradiation of ketones in 2-propanol to generate molecular hydrogen concurrent with net oxidation of the alcohol.[16] While the use of catalysts to accomplish net coupling of one-electron reagents to drive multielectron redox reactions remains an area of active investigation, a number of investigations have focused on the use of electrochemical cells to mediate similar conversions concurrent with the generation of a photocurrent.[2,17,18] In a recent communication we reported that reducing radicals such as the ketyl radicals and radical ions produced by electron-transfer quenching of excited states can be used to generate hydrogen in net photoelectrochemical processes.[2] In the present paper we report a more detailed account of this study which indicates that even with very simple electrochemical cells conventional photoreduction processes can be intercepted to drive reversible and endothermic reactions concurrent with moderately efficient generation of photocurrents. A very interesting aspect of the results obtained through this study is our finding that the reduced methyl viologen radical cation (via its dimer), used as an electron carrier in these studies, can enhance the overall efficiency obtained by self-sensitizing its own production from reductants such as 2-propanol and triethylamine.

Experimental Section

Materials. Benzophenone (Aldrich Chemical Co.) was recrystallized from acetonitrile. Triethylamine and diisopropylethylamine (Aldrich Chemical Co.) were vacuum distilled. 2-Propanol (Metheson Coleman & Bell), tetraethylammonium perchlorate (Eastman Kodak Co.), potassium chloride, pyridine, and perchloric acid (Fisher Scientific Co.) were used as received. All water was triply distilled. Tin porphyrin complexes were prepared and purified as reported in the literature.[19]

Photolysis Apparatus. The photolysis apparatus consisted of the following components. light source: 1000W Xenon-Mercury arc lamp with Schoeffel Instruments Corp. 2B LPS 255 power supply, coupled to a Bausch & Lomb high-intensity monochromater (Model No. 33-86-79 with 300-nm blaze) equipped with variable slits through an aluminum sleeve. The 7 in. long aluminum sleeve was machined to fit the system. The sample holder was mounted directly to the exit slit assembly. The sample holder is made of 2 in. × 0.75 in. wood machined to hold a 1-cm^2 cuvette in the light path. The block was mounted inside a wooden box (6 in. × 5 in. × 8 in., in 0.5 in. thick walls) which was placed in contact

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[†] Dedicated to George S. Hammond on the occasion of his 60th birthday.

(1) Address correspondence to this author.

(2) A preliminary communication of a portion of this work has appeared: Chandrasekaran, K.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5119.

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with the exit slit. The entire sample holder was painted black to minimize scattered light. A light shutter was fixed just inside the wooden box before the sample holder to control the time of illumination of the cell. Stirring was provided to the electrode compartments of the cell with a Tri-R magnetic stirrer (Model 19S T). The cells were not thermostated and the experiments were carried out at room temperature (~20 °C). Illumination by the monochromated light does not heat the cell compartment appreciably (<1 °C) during the time period of irradiation.

The Photoelectrochemical Cell. The cell used in these experiments consisted of three parts: A nonirradiated cathode compartment is equipped with a 4 × 1 cm platinum gauze or platinized platinum foil (4 × 1 cm) electrode along the sides of the cell wall. The cell is basically a 1 cm^2 glass tube fused to a 14/20 female joint with an inlet at a 45° angle fitted with a stopcock and a tube extending to the bottom of the cell to help bubble degassing. The photoanode compartment is again a 1 cm^2 Pyrex tube with a 4 × 1 cm platinum gauze electrode and two 4 × 1 cm^2 platinum foils fixed in the opposite faces of the cell. Light passed through the face of the cell and any light not absorbed is scattered by the wire gauze electrode and goes out of the cell compartment. This cell is also fused to a 14/20 female joint. The salt bridge consists of a 0.5 in. internal diameter glass tube fitted with a filling port and a pair of 14/20 male joints. Two glass frits of medium pore size were fixed at the tip of the salt bridge. The electrodes were cleaned with hexanes and then with 1 M aqueous hydrochloric acid. Then the clean electrodes were platinized as follows. The electrodes were immersed in a solution containing 10^{-2} M hexachloroplatinic acid and 10^{-4} M lead acetate. A current was passed through the solution from two alkaline batteries connected in series, using platinum wire as a reference electrode, until the electrodes turned black (~5 min). Then the electrodes were washed with triply distilled water several times. The electrodes were always kept immersed in water when not in use to avoid oxidation of the electrodes.

Electrolysis Solutions. Aqueous Systems. The cathode compartment contained 1.0 M aqueous perchloric acid solution. Solutions were not deaerated prior to use except for the experiments where quantitative hydrogen estimation was made. The photoanode solution contained the appropriate sensitizer—the concentrations were adjusted so that more than 99% of the irradiating light was absorbed unless otherwise indicated—dissolved in 1:1 v/v mixture of alcohol–water, where the alcohol was a hydrogen atom donor or in a 1:1 v/v mixture of water–acetonitrile. The water-soluble tin porphyrins were dissolved in a 4:1 v/v mixture of water–acetonitrile; 0.2 M potassium chloride was used as the supporting electrolyte.

The agar gelatin salt bridge was prepared by dissolving 9 g of potassium chloride in 30 mL of water. The potassium chloride solution was heated to boiling and 0.7 g of agar was added in several small portions with constant stirring. The resulting solution was transferred to the salt bridge while hot and cooled to room temperature by immersion in saturated aqueous potassium chloride solution. The salt bridge was always immersed in saturated aqueous potassium chloride solution when not in use.

Photocurrent Measurements. A typical experiment was done by filling the photoanode compartment with 0.1 M benzophenone, 0.01 M dimethyl viologen (*N*,*N*′-dimethyl-2,2′-bipyridine chloride salt), and 0.2 M potassium chloride in a 1:1 v/v mixture of 2-propanol and water. A stock solution was prepared and used repeatedly. Aging of the solution does not result in any difference in photocurrent measurements. Since, in this case, the components of the solution do not absorb visible light, exposing the aerated solution to the room light does not result in the buildup of photoproducts. The cathode compartment was filled with 1.0 M aqueous perchloric acid solution. The photoanode compartment was degassed by passing the deoxygenated nitrogen through the solution. The cells were stirred for about 15 min to stabilize the dark current; the sample shutter was opened, exposing the photoanode to 366-nm light, and the photocurrent noted. Photocurrents were measured with a microammeter (Keithley Instruments, Inc., Model No. 150B). The output from the microammeter was connected to a Hewlett-Packard X-Y recorder or readings were taken from the needle indicator. Photopotential measurements were made with a multi-volt meter built in this laboratory. A known amount of gas above the solution of the anode compartment was taken with a gas-tight syringe and analyzed in a gas chromatograph containing an alumina column immersed in a solution containing ethanol–dry ice. Argon at 50 PSI was used as the carrier gas. The peak heights were measured against standards. Conventional potassium ferrioxalate actinometry was used to determine the light intensity at the illuminating wavelength. The results were reproducible within experimental error (±10%).

Results

Benzophenone–Alcohol Studies. The cell schematically illustrated in Figure 1 was used in all the present experiments. In the studies with benzophenone and various alcohols both compartments contained partially aqueous solutions; in each case the dark cathode compartments contained 1.0 M perchloric acid. Consequently even in the dark there is a small potential and current flow (~5 μA) as a result of the pH gradient between the two cells. Since our previous studies had indicated that radical collection efficiencies were perhaps an efficiency-limiting factor,[2] the present photoanode compartment employs electrodes on three of the four faces of the cell so that only the entrance face is open.

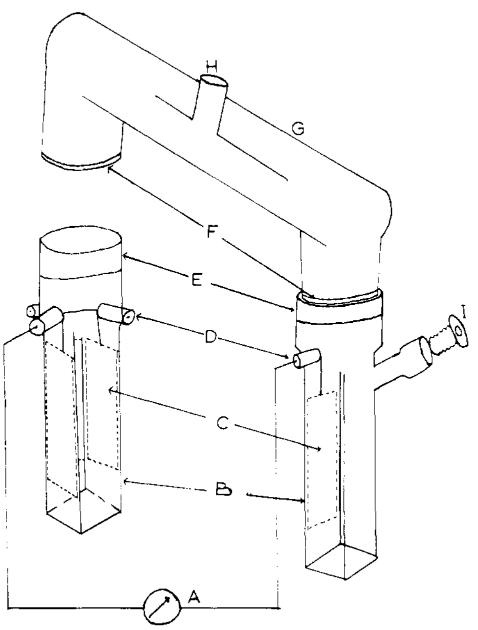

Figure 1. Photoelectrochemical cell used in these experiments. The left compartment is the illuminated anode cell while the right compartment is the dark cathode. The letters indicate the following: A, ammeter; B, square cuvettes; C, platinum electrodes; D, Ag epoxy support; E, 14/20 female joint; F, medium porous frits fixed to 14/20 male joints; G, salt bridge; H, filling port; I, threaded joint.

As has been well-documented in many previous studies, the photoreduction of ketones such as benzophenone by alcohols proceeds via ketyl radical formation (eq 1) and subsequent reactions (eq 2-5).[3-8] In the present photoelectrochemical experiments these subsequent rapid reactions of the ketyl radicals compete with anodic oxidation (eq 6 and 7) so that only a low

$$Ph_2C{=}O^* + R_1R_2CHOH \rightarrow Ph_2\dot{C}{-}OH + R_1R_2\dot{C}OH \tag{1}$$

$$R_1R_2\dot{C}OH + Ph_2C{=}O \rightarrow R_1R_2C{=}O + Ph_2\dot{C}{-}OH \tag{2}$$

$$2Ph_2\dot{C}{-}OH \rightarrow Ph_2C(OH){-}CPh_2(OH) \tag{3}$$

$$R_1R_2\dot{C}{-}OH + Ph_2\dot{C}{-}OH \rightarrow Ph_2CHOH + R_1R_2C{=}O \tag{4}$$

$$R_1R_2\dot{C}{-}OH + Ph_2\dot{C}{-}OH \rightarrow Ph_2C{=}O + R_1R_2CHOH \tag{5}$$

$$R_1R_2\dot{C}{-}OH \rightarrow R_1R_2C{=}O + H^+ + e^- \tag{6}$$

$$Ph_2\dot{C}{-}OH \rightarrow Ph_2C{=}O + H^+ + e^- \tag{7}$$

and unstable photocurrent (~25 μA) is obtained in each case; formation of solid benzopinacol can be observed in each case after only a few minutes of irradiation and the current decreases as the ketone is depleted. A drastic improvement in both the photocurrent obtained and cell stability can be effected by the addition of methyl viologen (MV^{2+}) (*N*,*N*′-dimethyl-4,4′-bipyridinium^{2+}) as a mediator (Figure 2). The interception of one or both ketyl radicals by MV^{2+} (eq 8 and 9) occurs efficiently with a resulting

$$Ph_2\dot{C}{-}OH + MV^{2+} \rightarrow Ph_2C{=}O + H^+ + MV^+ \tag{8}$$

$$R_1R_2\dot{C}{-}OH + MV^{2+} \rightarrow R_1R_2C{=}O + H^+ + MV^+ \tag{9}$$

suppression of benzpinacol formation;[14,20] in separate experiments

Table I. Photocurrents Generated for Cells Containing Benzophenone with Various Alcohols and Amines as Quenchers[e]

quencher	[concn], M	k_q, M^{-1} s^{-1} [c]	photo-current, μA	% efficiency,[d]
methanol[a]	12.6	3×10^5	162	20.0
ethanol[a]	8.6	6×10^5	343	42.5
2-propanol[a]	6.5	1×10^6	275	34.1
methylamine[b]	0.12	1×10^8	206	25.5
diethylamine[b]	0.025	$\sim 1 \times 10^8$	267	30.1
diisopropyl-ethylamine[b]	0.025	$\sim 1 \times 10^9$	384	47.6
triethylamine[b]	0.025	2×10^9	416	51.6
dimethylaniline[b]	0.025	3×10^9	399	49.5

[a] 1:1 water–quencher–alcohol v/v. [b] 1:1 water–acetonitrile v/v. [c] From: Turro, N.-J. "Modern Molecular Photochemistry"; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978. [d] Observed efficiency for electron flow (which is 1/2 the quantum efficiency since one photon produces two carriers [see text] under the experimental conditions). Benzophenone (0.1 M) absorbs more than 99% of light at the irradiation wavelength 366 nm and the quencher and mediator do not absorb. Under the experimental conditions all the excited states are quenched by the hydrogen-atom donor or electron donor but the net quantum yield for viologen radical generation varies (see text). [e] For all experiments the benzophenone concentration is 0.1 M and the dimethyl viologen (MV^{2+}) concentration is 0.01 M.

we have confirmed[14] that the initial quantum yield for formation of MV^+ in solutions of benzophenone (0.1 M), 2-propanol (6.5 M), and MV^{2+} (0.01 M) is 2.0 ± 0.2. Table I lists photocurrents and efficiencies of electron flow obtained for benzophenone with several alcohols as quenchers and MV^{2+} as a mediator. In each case evolution of hydrogen gas was observed in the dark cathode compartment; the quantum yield of hydrogen production measured for benzophenone–2-propanol in the prescence of MV^{2+} (0.27) agrees reasonably well with the measured photocurrent efficiency under the same conditions. Analysis of the gas over the anode compartment also revealed traces of hydrogen produced during the course of the irradiation; although quantitative determination could not be made, the yields compared to those produced at the dark cathode were much lower. Hydrogen could not be detected from either compartment in blank experiments carried out without irradiation.

The photocurrents obtained in unbuffered solutions are stable over several hours; however, prolonged irradiation (>24 h) results in a 50% decrease in the photocurrent together with a drop in pH from 4.6 to 2.0. For unbuffered solutions there is also a decrease in the viologen concentration over long irradiation periods; the turnover number of viologen obtained under these conditions is approximately 14. The use of solutions initially buffered to pH 7 results in more stable photocurrents; moreover, under these conditions no significant consumption of viologen is observed over 24 h. Benzophenone is not consumed under the conditions employed; the long wavelength spectra (above where acetone absorbs) are identical before and after irradiation. That the photocurrents produced are due to oxidation of the viologen radical (eq 10) is

$$MV^+ \rightarrow MV^{2+} + e \qquad (10)$$

indicated by the finding that concentrations of viologen radical equal to that obtained under steady-state photolysis conditions give the same initial current when the circuit is completed in the dark. The dark current under these conditions decreases with approximately the same profile as that observed by shutting off the light as indicated in Figure 2 for the photochemical experiments.

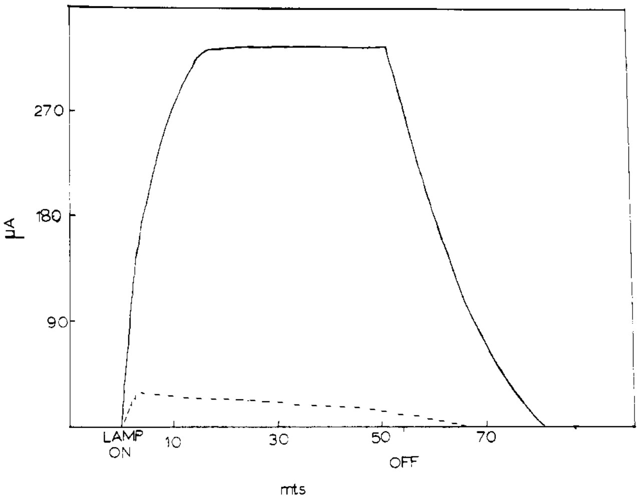

Figure 2. Photocurrent time profile for benzophenone–2-propanol solutions (—) with methyl viologen as a mediator (---) with no added viologen.

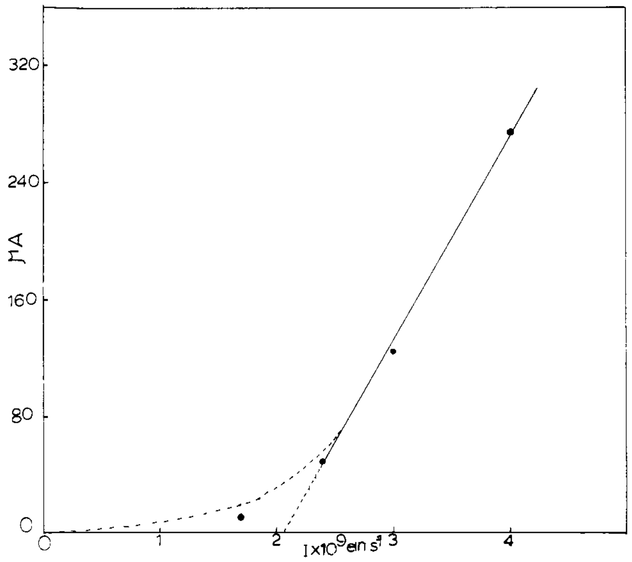

Figure 3. Photocurrent vs. light intensity for the system benzophenone–2-propanol–MV^{2+}. The ordinate is the measured photocurrent while the abscissa is the absorbed light intensity at 366 nm.

The current produced in the photoelectrochemical experiments with benzophenone–2-propanol–MV^{2+} at 366 nm shows a strong dependence on light intensity (Figure 3). While there is very little current produced at low light intensities, the current is observed to be linear with light intensity above a threshold (for this system and cell, 2.15×10^{-9} einstein/s). If this "threshold" intensity is subtracted from the true intensity, a "corrected" plot gives a direct proportionality between the photocurrent and intensity.

In the experiments at 366 nm where moderate light intensities produce the highest photocurrents observed (and consequently the highest quantum efficiency, $\phi_e = 0.64$ or 32% of the maximum efficiency), the steady-state concentration of MV^+ can be determined to be 0.0009 M. This value is relatively high (the solution is visibly violet) and in fact indicates that an appreciable fraction of the incident light at 366 nm is absorbed by MV^+; calculation based on the initial concentration of benzophenone indicates that the former absorbs only 18.5% of the light while the remainder activates either MV^+ or its dimer MV_2^{2+}. Since the steady-state photocurrent efficiency is greater than the fraction of light ab-

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(20) Benzophenone[2,21] as well as a number of other excited states[22,23] are quenched by electron transfer to MV^{2+} with varying efficiency. Our results[2] suggest direct quenching of benzophenone should not be very important; the much higher quenching rates reported by Das[21] in other solvents suggest that quenching of the triplet could be a significant path in the present system. While it is easy to envision a plausible mechanism for the net chemical conversion observed proceeding via the path, Das' indication that electron-transfer quenching is only ca. 60% efficient would be inconsistent with our measured value, $\phi_{MV^+} \approx 2$.

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Table II. Photopotentials and Photocurrents Generated in Benzophenone-Sensitized Reactions

quencher	photo-potential, mV	photo-current, μA
$(C_2H_5)_3N$[a]	664	232
DIPEA[a]	719	220
2-propanol[b]	624[c]	275[c]

[a] Acetonitrile-water mixture used as solvent; DIPEA = diisopropylethylamine. [b] 2-Propanol-Water mixture used as solvent. [c] Measured in the presence of 10 mM MV^{2+} [benzophenone] = 0.1 M; [KCl] = 0.2 M.

Table III. Effect of pH on Photocurrent in the Benzophenone-2-Propanol-MV^{2+} System[a]

medium	photo-current, μA
neutral	275
0.001 M KOH	405
0.010 M KOH	536
0.10 M KOH	285

[a] [Benzophenone] = 0.1 M; [2-propanol] = 6.5 M; [PQ^{2+}] = 0.010 M; ionic strength adjusted with KCl so that final ionic strength is 0.2; irradiated at 366 nm. Light intensity 4.03 × 10^{-9} einstein/s.

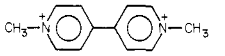
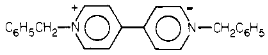
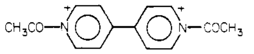
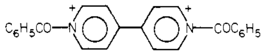
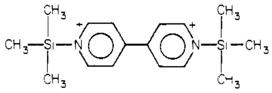
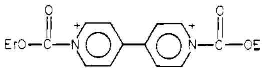
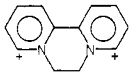
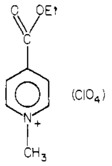
sorbed by benzophenone and since sensitization of benzophenone by energy transfer from excited states of MV^+ or MV_2^{2+} should be highly unlikely, there appears to be clear indication that additional photochemical reactions involving excited states of the reduced viologen are contributing to the photocurrent produced.

Electrochemical reduction (465 mV) of MV^{2+} to produce partial conversion to MV^+ and its dimer MV_2^{2+} was carried out in 1:1 water-2-propanol (nitrogen deaerated).[24] The solution was disconnected from the electrochemical apparatus and irradiated at 366 nm; under these conditions a steady increase in the concentration of MV^+ was observed thus indicating that MV^+ (or the dimer, MV_2^{2+}) can self-sensitize its formation in the presence of 2-propanol (no reaction is observed when water alone is present).[24] While the mechanism of this process will be discussed later (see Discussion), the self-sensitization process is clearly a key step in the generation of moderately efficient photocurrents in all of the systems investigated. The fact that this process occurs with lower efficiency than the production of MV^+ in the benzophenone-2-propanol photolysis explains the slow photocurrent decay observed at wavelengths where only MV^+ absorbs.

As data in Table II indicate, moderate photopotentials in the range of 600-700 mV were obtained for the various systems employed, using benzophenone as the initial photoexcited sensitizer. For the benzophenone-2-propanol-MV^{2+} system the photocurrent was found to increase with increasing pH up to pH 12 as indicated in Table III. For 0.1 M KOH there is dark reaction between MV^{2+} and OH^- that results in a colored solution which upon irradiation results in less excitation of benzophenone. For this system it was found that MV^{2+} could be replaced by a number of viologen derivatives having differing reduction potentials; Table IV lists values of photocurrents obtained for 366-nm irradiation together with net efficiencies calculated from the current flow. As the data indicate, while several dications gave comparable or even higher currents than MV^{2+}, the monopyridinium ions such as 4-cyano-*N*-methylpyridinium gave relatively low photocurrents under these conditions

The long-term stability of the various viologen derivatives listed in Table IV has not been investigated; certainly some hydrolysis of the acylpyridinium derivatives would be anticipated at low or high pH. In the present studies involving neutral pH solutions, stability was not a problem for short irradiation times.

Table IV. Applications of Various Weitz-Type Mediators in the Benzophenone-2-Propanol Reaction[d]

mediator[a]	photocurrent, μA	efficiency[b]	E_{red}[c]
	275	34.1	−0.26
	245	30.4	−0.19
	283	35.1	+0.25
	330	40.9	+0.32
	240	29.8	−0.45
	265	32.8	+0.35
	285	35.4	−0.8
p-cyano-*N*-methylpyridinium	51	6.3	−0.9
	41	5.0	

[a] [Mediator] = 0.01 M. (All the mediators used are chloride salts unless mentioned otherwise. [b] Observed quantum yield for electron flow under the experimental conditions described. [c] From ref 42. [d] Experimental conditions: [benzophenone] = 0.1 M; solvent 1:1 2-propanol-water v/v mixture; 0.2 M potassium chloride supporting electrolyte.

Table V. Photocurrents Generated from Tin Porphyrin-Triethylamine Solutions at Various Wavelengths[a]

mediator added	λ, nm	photo-current, μA
none	420	16.5
MV^{2+}, 0.01 M	420	132
MV^{2+}, 0.01 M	405	120
MV^{2+}, 0.01 M	436	130
MV^{2+}, 0.01 M	546	110
MV^{2+}, 0.01 M	578	112

[a] Porphyrin concentration ~4 × 10^{-5} M (all light absorbed); [$(C_2H_5)_3N$:] = 0.025 M.

Benzophenone-Amine Studies. It has been well documented that excited states of benzophenone and other ketones are quenched efficiently by amines such as triethylamine in processes involving electron transfer (eq 11).[9-11,23] In many cases subsequent

$$Ph_2C{=}O^* + Et_3N{:} \rightarrow Ph_2\dot{C}{-}\ddot{O}{:}^- + Et_3N^{+\cdot} \qquad (11)$$

$$Ph_2\dot{C}{-}\ddot{O}{:}^- + CH_3CH_2\dot{N}^+Et_2 \rightarrow Ph_2\dot{C}{-}OH + CH_3\dot{C}H\ddot{N}Et_2 \qquad (12)$$

proton transfer (eq 12) results in formation of ketyl radicals and the corresponding free radical from the amine. These radicals are both reducing radicals and it would be anticipated that scavenging of them by an oxidant such as MV^{2+} should also occur with high efficiency. Consequently it was not surprising to observe that even though the net quantum efficiency for ketone disappearance in the presence of Et_3N: is only 0.2,[10] addition of MV^{2+} results in an initial quantum efficiency for viologen reduction comparable to that observed in the benzophenone-2-propanol-MV^{2+} studies.

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(24) Irradiation of MV^+ produced by sodium dithionite reduction of MV^{2+} in 2-propanol-water leads to decrease in the [MV^+] while no reaction is observed with water alone as the solvent. The dithionite or its redox products may be scavenging radicals produced in the reaction.[25]

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Table VI. Evaluation of Energy Input–Output Relationships for the Photoelectrochemical Systems Employed with Benzophenone and Tin Porphyrins

system	λ_{ex}, nm	input, mW	output, mW		% efficiency
			electricity	endothermic reaction	
benzophenone-2-propanol-MV^{2+}	366	1.308	0.172	0.052	17
benzophenone-triethylamine-MV^{2+}	366	1.308	0.260	0.097	27
$SnPCl_2{}^{4+}$-triethylamine-MV^{2+}	436	0.758	0.081	0.031	15

As data in Table I indicate, irradiation of benzophenone–MV^{2+} in the presence of several amines in the cell illustrated in Figure 1 leads to the generation of steady photocurrents with moderate overall efficiency. The relationship between photocurrent and absorbed light intensity for the system is similar to that observed (shown in Figure 3) for the benzophenone–2-propanol–MV^{2+} system. In the case of benzophenone–triethylamine–MV^{2+} quantitative analysis of the gas evolved in the dark cathode compartment indicated hydrogen production with an overall efficiency of 0.44, slightly lower than that expected based on the photocurrent generated. Here again the steady-state concentrations of MV^+ produced are clearly high enough such that a major fraction of the light is absorbed by MV^+ or the dimer $MV_2{}^{2+}$. Consequently in these systems a self-sensitization of MV^+ formation by triethylamine reduction must be occurring as was discussed above for 2-propanol.

Tin Porphyrin–Triethylamine Systems. While the above-described systems based on benzophenone generally employ ultraviolet excitation, at least to initiate the photocurrent generation, it is clear that a number of visible light-absorbing chromophores can generate similar radicals by hydrogen-atom or electron-transfer processes. Consequently it should be possible to use a variety of sensitizers in comparable reactions in which mediators such as MV^{2+} are reduced and in which their reduction products can participate in self-sensitization reactions. While we are still in the process of studying a number of systems, sufficient data on one such system are available to include in this study as a comparison to the benzophenone based system.

Previously we and others have shown that a wide variety of metalloporphyrins can be photoreduced by amines and other reductants to yield sequentially chlorins and isobacteriochlorins.[27–34] These reactions usually occur by electron-transfer processes analogous to those outlined for benzophenone in eq 11 and 12; subsequent combination of the two radicals yields reductive adducts in the case of metalloporphyrins and tertiary amines, although the intermediates can be diverted in some cases.[33] In the present studies we have employed the tin(IV) complex of *meso*-tetrakis(*p*-*N*-methylpyridyl)porphyrin, $SnPCl_2{}^{4+}$. Irradiation of the porphyrin in the presence of triethylamine in the cell shown in Figure 1 results in low photocurrent (Table V). The system does not produce the normal photoproducts observed for irradiation of porphyrins with amines; however, the reduced porphyrin is evidently not rapidly oxidized at the electrode and the solution is observed to turn from violet to yellow on irradiation. In the dark the violet color of the starting porphyrin is regenerated; absorption spectra taken before and after irradiation indicate no net consumption of the porphyrin. Presumably the low steady photocurrent obtained is attributable at least partially to internal filtering by the reduced porphyrin.

Addition of MV^{2+} as a mediator in the porphyrin–triethylamine system results in a nearly tenfold increase in the steady photocurrent obtained (Table V). Although the photocurrents obtained with this system are substantially lower than those obtained with the benzophenone-based reactions, it is noteworthy that photocurrents of more than 100 μA are obtained with visible light of wavelengths up to 578 nm. While this system has not been as extensively investigated as those using benzophenone and turnover numbers for MV^{2+} have not been determined, the porphyrin sensitizer has been found to be stable over moderate (>2 h) periods of irradiation.

Discussion

The results presented above indicate that several well-studied photoprocesses initiated via hydrogen-atom abstraction or one-electron transfer can be channeled through photoelectrochemical cells to give moderately efficient photocurrents and to drive an endothermic net chemical conversion. The overall reaction in the benzophenone–2-propanol system is of course that given by eq 13. for the systems using trimethylamine in the presence of water

$$CH_3C(OH)HCH_3 \rightarrow CH_3C(=O)CH_3 + H_2 \qquad (13)$$

the net reaction is given by eq 14.[35,36] The former reaction is

$$(C_2H_5)_3N + H_2O \rightarrow CH_3CHO + (C_2H_5)_2NH + H_2 \qquad (14)$$

endothermic by 21.5 kcal/mol while the latter is endothermic by 27.3 kcal/mol (both calculated from heats of formation of the pure liquids).[37] However, in both cases the net endothermicity of the overall reaction as carried out is somewhat lower; this is due to the fact that the occurrence of reactions 13 and 14 is accompanied in each case by the effective transfer of protons from the acid compartment (the dark cathode) to the higher pH anode compartment. A simple Nernst equation calculation indicates this reaction has $\Delta G^\circ \simeq -12.5$ to -16 kcal/mol of H_2. With use of these values, the measured photocurrents and potentials, the quantum efficiencies, and the measured light intensities, it is possible to calculate an energy balance for the cells. Thus Table VI lists the energy input, electricity produced, chemical energy stored, and overall efficiency considering both processes. The values, which range from 14 to 27% in the three cases measured, are reasonable; although the photochemical steps and subsequent processes occur with high efficiencies the various steps all involve energy losses, and there are clearly some losses associated with the electrode processes and cell design. It is interesting that in each case the much larger fraction of the energy captured is in the electricity produced even though each reaction is clearly endothermic.

The original objective in using the benzophenone–2-propanol–methylviologen system with incident light at 366 nm was simply to employ a system that was both well-defined chemically and highly efficient to determine what level of efficiency could be obtained in a photoelectrochemical cell based on solution photochemical reactions. A cell based on a reaction such as eq 13 is particularly appealing for these studies since the products are relatively stable and the reaction should be readily reversible under a variety of conditions. In fact it should be possible to reverse reaction 13 in an electrochemical cell although we have

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not yet attempted this. The initial reaction sequence anticipated for this cell consisted of eq 1, 2, and 8–10 in the photoanode compartment. Since reactions 1, 8, and 9 occur with high efficiency[14] we anticipated that the reduced viologen MV^+ should accumulate at any light intensity until a sufficient $[MV^+]/[MV^{2+}]$ gradient to drive the electrochemical reduction of protons in the dark cathode was obtained. This would of course lead to the prediction of a direct relationship between adsorbed light intensity (corrected for the fraction absorbed by MV^+) and photocurrent. That such a relationship is not observed (Figure 3) until a "threshold" intensity is attained appears likely to be due to oxidation of MV^+ at lower $[MV^+]$ by processes not effective in generating a photocurrent. One such process is direct oxidation concurrent with hydrogen generation at the platinum anode. This reaction concomitant with reduction of the aromatic ring of the viologen has been observed for aqueous viologen solutions with a variety of platinum catalysts.[38–40] Since we have observed the photoproduction of at least traces of hydrogen in the anode compartment as well as some disappearance of viologen in these studies, it is reasonable to conclude that some inefficiency due to this type of short-circuiting occurs in the present cell, particularly at lower light intensities.

The observation that fairly high concentrations of MV^+ must be attained before efficient current flow occurs would be expected to result in extremely low efficiencies for the benzophenone-based systems if all effective excitation were to result only from light absorbed by benzophenone, since MV^+ absorbs strongly ($\epsilon \sim 14\,000$) at 366 nm.[41] The observation that overall efficiencies are in fact higher under steady-state conditions than would be predicted based on the fraction of light absorbed by benzophenone led to the unexpected but welcome discovery of MV^+ can sensitize its own production from MV^{2+} in the presence of 2-propanol or triethylamine. This reaction, precise details of which are currently under investigation with MV^+ and a variety of other Weitz-type radicals,[42] could involve either or both MV^+ and the dimer MV_2^{2+}, since appreciable concentrations of both species are present at the concentrations employed.[41] Preliminary studies of irradiation of MV^+ in the presence of 2-propanol suggest that the efficiency of the reaction is relatively low ($\phi_{MV^+} \sim 0.1$ at 366 nm); a study of wavelength and concentration effects indicates that only activation of the dimer, MV_2^{2+}, at $\lambda \leq 366$ nm is effective. The self-sensitization by viologen involving the dimer can be proposed as reasonably occurring by the sequence of reactions given by eq 15–18 in the presence of 2-propanol and by eq 15, 17, and 19–21

$$MV_2^{2+} \xrightarrow{h\nu} MV_2^{2+*} \tag{15}$$

$$MV_2^{2+*} + CH_3C(OH)HCH_3 \rightarrow MV_2^+ + CH_3\underset{\bullet}{C}(OH){-}CH_3 + H^+ \tag{16}$$

$$MV_2^+ + MV^{2+} \rightarrow MV_2^{2+} + MV^+ \tag{17}$$

$$CH_3{-}\dot{C}(OH){-}CH_3 + MV^{2+} \rightarrow MV^+ + CH_3C({=}O)CH_3 \tag{18}$$

$$MV_2^{2+*} + Et_3N: \rightarrow MV_2^+ + Et_3N^{+\cdot} \tag{19}$$

$$Et_3N^{+\cdot} + Et_3N: \rightarrow Et_3NH^+ + CH_3\dot{C}H\dot{N}\dot{E}t_2 \tag{20}$$

$$CH_3\dot{C}H\dot{N}\dot{E}t_2 + MV^{2+} \rightarrow CH_3CH{=}NEt_2 + MV^+ \tag{21}$$

in the presence of triethylamine. Both reduction steps 16 and 19 are reasonable since the second reduction of the monomer requires only ~0.4 V and the viologen dimer excited state energy is >30 kcal/mol. Equation 17 is analogous to conproportionation of doubly reduced viologen and MV^{2+}, a process which is highly favored.[42] The self-sensitization process would be expected to yield a net maximum quantum yield of 2; a number of potential sources of inefficiency in the quenching processes and subsequent reactions exist. The key finding here is the possibility that self-sensitization of MV_2^{2+} (or the monomer in other cases) or a related semireduced Weitz-type species, having similar broad-spectrum visible light absorbing characteristics but higher efficiencies for the reaction, can greatly extend both the wavelength response and the net efficiency of these cells. The moderate efficiencies obtained by using monochromatic light and the fairly simple systems described herein suggest that a wide variety of possibilities exist for the construction of useful solution-based photoelectrochemical cells using these and related reactions.

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