consistent with the supposition that the isomerization mechanisms of the two radical anions are different, the process (1)⁻· → (2)⁻· probably involving a metal–hydride intermediate,[3] and (3)⁻· → (4)⁻· proceeding through a "simple" structural deformation.[17]

The heterogeneous charge-transfer rate of the 1,5-isomer, k_s^{app} = 0.06 cm s⁻¹, is somewhat lower than that of the 1,3-isomer, 0.28 cm s⁻¹, and that reported for the 1,3-isomer of (COT)Fe(CO)₃, 0.24 cm s⁻¹. It is expected that stereochemical changes during reduction will lower the electron-transfer rate,[2a,19] as predicted by the Marcus theory of electron transfer.[20] The lower electron-transfer rate for the tub-shaped 1,5-isomer may be viewed in this context as arising from structural deformations occurring during the reduction of (3) to its anion radical. Since the isomerization of (3)⁻ to the 1,3-isomer is so facile, it may be that in the initial reduction step, (3) deforms part way to the chair conformation of (4)⁻. Whatever the transition-state structure involved in the heterogeneous reduction of (3), the activation barrier to its formation is not large, since the k_s^{app} value of 0.06 cm s⁻¹ is still fairly high, falling in the upper end of values associated with quasi-reversible processes.

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Solar Energy Conversion through Ligand Photodissociation
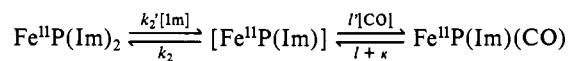
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Abstract: We examine a new technique for photochemical conversion of solar energy based on ligand photodissociation from metal complexes. We illustrate the concept with a photogalvanic cell in which voltages are generated by photodissociation of CO from carbonylferroheme and with a cell in which the illuminated electrode is coated with an iron tetraphenylporphyrin.

Research on the conversion of sunlight into heat, electricity, and burnable fuels has accelerated in recent years.[1] We here discuss the possibility of a new technique for photochemical conversion of solar energy, one based on ligand photodissociation from metal complexes.[2] The concept is illustrated with a photogalvanic cell[1a,e] in which voltages are generated by the photodissociation of CO from carbonyl ferroporphyrins.[3] We also report a cell in which the carbonyl ferroporphyrin is coated on an optically transparent electrode.

Ligand photodissociation can form the basis of a solar cell if light can appreciably perturb the ligation equilibrium in the vicinity of an illuminated electrode. For example, a cell with one illuminated and one dark electrode and containing a dissolved photodissociable complex will behave as a photogalvanic cell. Bonaventura et al.[4] have shown that the CO binding by illuminated myoglobin can be described by a light-dependent equilibrium constant. Similarly, CO binding to an iron porphyrin such as Fe^IIP[5] near an electrode in the presence of excess imidazole and CO can be represented by Scheme I, where the bracket indicates

Scheme I

$$\text{Fe}^{II}\text{P(Im)}_2 \underset{k_2}{\overset{k_2'[\text{Im}]}{\rightleftharpoons}} [\text{Fe}^{II}\text{P(Im)}] \underset{l+\kappa}{\overset{l'[\text{CO}]}{\rightleftharpoons}} \text{Fe}^{II}\text{P(Im)(CO)}$$

that the concentration of the five-coordinate Fe^IIP(Im) is very low if [Im] > 0.25 M. Under illumination, *l*, the dark rate constant for release of CO by the six-coordinate Fe^IIP(Im)(CO), is augmented by the CO photodissociation rate, κ, which is proportional to the intensity of the actinic light: $\kappa \propto I$. The ratio of concentrations between the bis(imidazole) and CO-bound species is then light dependent:

$$\frac{[\text{Fe}^{II}\text{P(Im)}_2]}{[\text{Fe}^{II}\text{P(Im)(CO)}]} \cong \frac{(l+\kappa)k_2'}{l'k_2}\frac{[\text{Im}]}{[\text{CO}]} \cong \frac{K_2[\text{Im}]}{L(I)[\text{CO}]} \quad (1)$$

where $K_2 = k_2'/k_2$ is the equilibrium constant for binding the second imidazole and $L(I) = l'/(l+\kappa)$ is the apparent equilibrium constant for CO binding under illumination; $L_0 = l'/l$ is the dark value. The potential of the illuminated electrode will vary with *I* insofar as this ratio (eq 1) deviates from its dark value. Metal complexes such as the ferroporphyrins are particularly intriguing for light-harvesting applications because of their broad and intense absorption envelope[6] and because the quantum yield for CO dissociation is essentially unity over the entire envelope.[3] Moreover, CO dissociations occur within 1 ps after excitation, and thus the dissociation process is not susceptible to quenching.[7]

Experimental Methods

The electrochemical cell for measurement of photovoltages (ΔV_P) typically employed an illuminated working electrode of optically trans-

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(5) Abbreviations: FeP, iron protoporphyrin IX; Im, imidazole; I_0, maximum light intensity; *I*, incident light intensity; TPP, tetraphenylporphinato.

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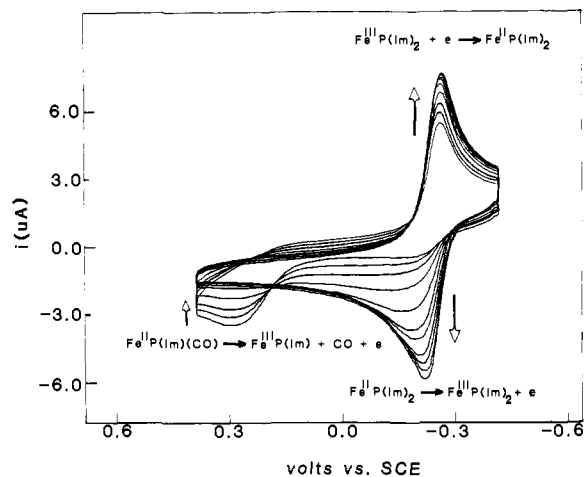(7) Shank, C. V.; Ippen, E. P.; Berson, R. *Science (Washington, D.C.)* **1976**, *193*, 50–51.

Figure 1. Steady-state cyclic voltammograms of a heme–Im solution under CO at an illuminated SnO_2 OTE. Arrows in the figure indicate increasing light intensity. Conditions: 3.69 M imidazole, pH 7.38, 1 atm of CO, total heme 468 μM, approximately 50% ferroheme and 50% ferriheme (reduction of ferriheme to ferroheme was accomplished electrolytically), 70/30 (v/v) methanol/H_2O solvent. The reference was a saturated calomel electrode.

parent, fluoride-doped ($10^{22}/cm^3$) SnO_2; experiments were also performed with a Pt foil. The dark auxiliary electrode was Pt and the reference either a SSCE or Pt wire pseudoreference. A stock solution of $Fe^{III}P(Im)_2Cl$ was prepared by adding recrystallized $Fe^{III}PCl^{8a}$ to a 70/30 $MeOH/H_2O$ (v/v) solvent containing 0.1 M TEAP and a known amount of imidazole and was adjusted to a neutral pH with HCl. Any undissolved solid was removed by filtration, and the evaporation of MeOH during filtration (3–5% of total volume) was corrected. The final concentration of $Fe^{III}P$, typically 0.3 mM, was determined spectrophotometrically (ϵ = 10.5 mM^{-1} cm^{-1} at 530 nm for $Fe^{III}P(Im)_2Cl^{8b}$). CO was first passed through a Ridox (Fisher) column, then was bubbled through solvent, and finally was bubbled into the electrochemical cell containing the reagent solution. Normally, after 1 h of CO bubbling, microliter quantities of dithionite solution in degassed H_2O were injected through a rubber septum to obtain the desired ratio of $Fe^{III}P(Im)_2Cl$ to $Fe^{II}P(Im)(CO)$, the reduction being followed spectrophotometrically. Electrochemical reduction gave the same results. The dark equilibrium constants (eq 1) have values L_0 = 4.8 × 10^8 M^{-1} [9] and $K_2 \approx$ 33 M^{-1}.[10] Thus, in the dark and for the conditions normally employed (0.01 atm < $P(CO)$ < 1 atm, 0.007 M < [Im] < 4 M), essentially all ferroheme was in the form $Fe^{II}P(Im)(CO)$.

Experiments were also performed with iron porphyrin coated onto a SnO_2 OTE. $Fe^{III}TPPPCl$ was dissolved in CH_2Cl_2, 2 mM in imidazole, and the $Fe^{III}TPP(Im)_2Cl$ formed was spin coated on a clean SnO_2 OTE to a thickness of ca. 85 Å as determined spectrophotometrically.[8c] The spin-coated SnO_2 electrode was the working electrode of a cell whose electrolyte solution consisted of 1 M imidazole and 0.1 M TEAP in H_2O titrated to pH ~7.0 with HCl and was saturated with CO. The $Fe^{III}TPP(Im)_2Cl$ film could be quantitatively reduced to $Fe^{II}TPP(Im)$-(CO) by a single cathodic sweep.

The light source was an Oriel Co. 360-W Hg–Xe arc lamp equipped with a water filter and screened by a long-wavelength pass filter with a nominal cutoff of 360 nm (Corning no. 4-96). The cell illumination was varied by using additional neutral density filters (Melles-Griot) to reduce the maximum intensity (I_0). Photovoltages were measured with a high-impedance electrometer; cyclic voltammograms were obtained with a Bioanalytical Systems Inc. DCV-4 voltammetry control unit.

Results

In order to monitor the concentration of the various FeP species at an illuminated SnO_2 electrode–solution interface, we employed cyclic voltammentry,[12,13] since optical methods are difficult to apply
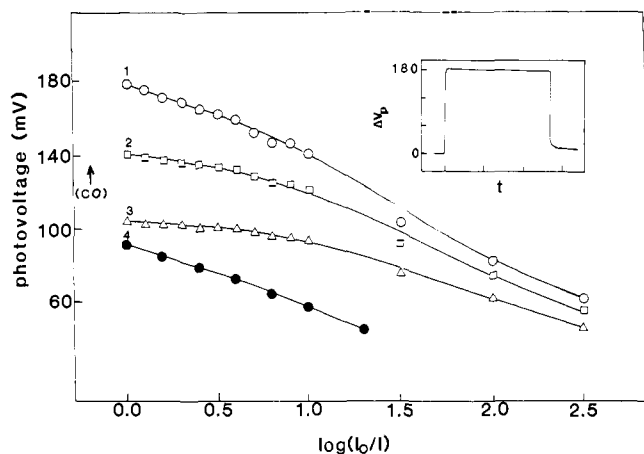

Figure 2. Photovoltage vs. the ratio of the maximum light intensity, I_0, to the incident intensity, I, at the SnO_2 OTE–solution interface. Curves 1–3 employ a $Fe^{II}P(Im)(CO)$ solution comprised of 70/30 (v/v) $MeOH/H_2O$ solvent, pH 6.96, 784 mM imidazole, 149 μM ferroheme, 59.0 μM ferriheme: curve 1, 1 atm of CO; curve 2, 0.05 atm of CO; curve 3, 0.01 atm of CO. Curve 4 employs a SnO_2 OTE that was spin coated with a $Fe^{III}TPP(Im)_2Cl$ to a thickness of ca. 85 Å. Electrolyte solution: 1.14 M aqueous imidazole, pH 7.01, 1 atm of CO. $Fe^{III}TPP$-$(Im)_2$ was reduced to $Fe^{II}TPPImCO$ in a single cathodic sweep during cyclic voltammetry. Lines in the figure serve merely to aid the eye. Inset: photovoltage (mV) vs. time (min) plot for photogalvanic cell. Conditions: 2.05 M imidazole, 1 atm of CO, pH 7.12, 250 μM ferroheme 223 μM ferriheme.

at high FeP concentrations. Figure 1 presents steady-state cyclic voltammograms of a solution that, in the absence of light, has a composition of 50% $Fe^{III}P(Im)_2$ and 50% $Fe^{II}P(Im)(CO)$; no other heme complex is of significant concentration. The cathodic wave in the dark cyclic represents the electrochemically reversible[13] reduction

$$Fe^{III}P(Im)_2 \xrightarrow{e^-} Fe^{II}P(Im)_2$$
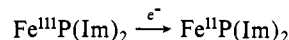
There is no matching reoxidation wave because ligand exchange to form $Fe^{II}P(Im)(CO)$ is rapid and complete. The oxidation of $Fe^{II}P(Im)(CO)$ is highly electrochemically irreversible[14] and is only observed at a potential 0.6 V more positive than $Fe^{II}P(Im)_2$ oxidation. As light of progressively greater intensity is applied to the SnO_2 electrode, the anodic current associated with $Fe^{II}P$-$(Im)(CO)$ oxidation decreases, a peak associated with the oxidation of $Fe^{II}P(Im)_2$ grows in, and the cathodic current increases. With the maximum light intensity available, the cyclic voltammogram is essentially that of the reversible $Fe^{III}P(Im)_2$–$Fe^{II}P(Im)_2$ couple in the absence of CO; cathodic and anodic waves are symmetric about the redox potential of the couple and are separated by only slightly more than the ideal value of 59 mV.[12] Figure 1 thus shows that the dark equilibrium of eq 1 lies far toward $Fe^{II}P(Im)(CO)$, but under illumination the equilibrium is shifted far toward $Fe^{II}P(Im)_2$, as would be required for the generation of a photovoltage. Note also that the anodic wave observed under illumination corresponds to a large, transient photocurrent.

The changes in ligation equilibrium produced by illuminating the SnO_2 electrode indeed give rise to a photovoltage, as shown in Figure 2. The illuminated electrode is negative, and for [Im] > 50 mM and $P(CO)$ = 1 atm the rise and fall of the open circuit photovoltage coincide with the shutter and drift is minimal (Figure 2, inset). At lower imidazole concentrations, overshoots in the photovoltages, well-known in other photogalvanic systems,[11] are

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observed. The voltages are independent of the ratio of ferro to ferriheme and of the total heme concentration for the values explored, namely, $^1/_4 < [Fe^{II}P]_{tot}/[Fe^{III}P]_{tot} < 10$ and 0.2 mM $< [FeP]_{tot} < 0.5$ mM. The observed photoeffect does *not* require a semiconductor electrode. Comparable voltages are observed when a Pt foil electrode is illuminated. Moreover, no voltage occurs when a solution without CO was illuminated. Thus, the photovoltage in fact arises from a light-induced perturbation of the CO-binding equilibrium of Scheme I. The photovoltage decreases with [Im] and increases with $P(CO)$ and with the light intensity (decreasing filter absorbance; Figure 2). For $P(CO)$ = 0.01 atm, approach to the saturating value of $\Delta V_P \sim 100$ mV is clearly seen by $I \sim I_0/10$, whereas at full available light intensity the photovoltage of the cell with $P(CO)$ = 1 atm is much larger, $\Delta V_P \sim 200$ mV, and is well below light saturation.

Experiments were also performed on the iron porphyrin coated SnO_2 OTE. Illumination of an electrode whose film had been quantitatively reduced to $Fe^{II}TPP(Im)(CO)$ gave unstable photovoltages. If the film contained finite proportions of the Fe^{III} TPP, a stable photovoltage was obtained having light dependence and limited $\Delta V_P \sim 100$ mV such as that in Figure 2.

Discussion

The results presented here show that a photoinduced alteration in the ligand equilibrium of a ferroporphyrin gives rise to an appreciable photovoltage. The following model is consistent with these results. Since the oxidation of $Fe^{II}P(Im)(CO)$ is highly irreversible and occurs at a very positive potential, the half-cell potential of the dark electrode is set by the dark concentration ratio $([Fe^{III}P(Im)_2]/[Fe^{II}P(Im)_2])_{dark}$, and that of the illuminated electrode by the concentration ratio $([Fe^{III}P(Im)_2]/[Fe^{II}P-(Im)_2])_{light}$, at the electrode surface. As a consequence, an illuminated cell under open-circuit conditions should generate a photovoltage that depends parametrically on the light intensity through the equation

$$\Delta V_P = -0.059 \log \frac{[(Fe^{II}P(Im)_2)]_{light}}{[(Fe^{II}P(Im)_2)]_{dark}} \quad (2)$$

which is independent of $[Fe^{III}P(Im)_2]$. For high [Im] and [CO], where Scheme I applies, this can be rewritten in terms of the ligation equilibrium parameters

$$\Delta V_P^L = -0.059 \log \frac{1 + L_0[CO]/K_2[Im]}{1 + L(I)[CO]/K_2[Im]} \quad (3)$$

In particular eq 3 shows that ΔV_P should reach a limiting value with increasing light intensity:

$$\Delta V_P = -0.059 \log \frac{[Fe^{II}P]_{total}}{[Fe^{II}P(Im)_2]_{dark}} = -0.059 \log \frac{L_0[CO]}{K_2[Im]} \quad (4)$$

The analysis is in qualitative agreement with the overall behavior of ΔV_P as $P(CO)$, light intensity (Figure 2), and [Im] vary. Also, the peak currents of the cyclic voltammogram from an illuminated cell qualitatively correspond with the observed ΔV_P. However, a rigorous, quantitative treatment of the cyclic voltammogram under illumination is not yet available, and we therefore defer attempts to apply 2 directly.

The observations of photovoltages from a carbonylferroporphyrin photogalvanic cell clearly validate our initial premise. Of course, other complexes must be examined and photocurrent measurements performed.

Thermodynamics of Homoantiaromaticity and Homoaromaticity: Homo[8]annulene and Its Dianion

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Abstract: Calorimetric techniques were used to find that the heat of formation of the homoaromatic homo[8]annulene dianion potassium salt from potassium metal and *cis*-bicyclo[6.1.0]nona-2,4,6-triene (CBN) is very close to zero. The very low
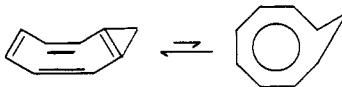
thermodynamic stability of this homoaromatic system relative to that for the aromatic cyclooctatetraene dianion was found to be due to the large electron–electron repulsion in the homoaromatic dianion, the low electron affinity of CBN, and the fact that the protruding methylene group perturbs the crystal lattice. The equilibrium constant controlling the electron transfer from the anthracene anion radical to CNB in dimethoxyethane to yield the homo[8]annulene anion radical and anthracene was studied as a function of temperature by using ESR techniques. The enthalpy of this electron-transfer reaction was used in a thermochemical cycle to obtain the electron affinity of CBN. Further, the heat of tautomerization of CBN to the homoantiaromatic open structure has been estimated to be about 32 kcal/mol.

The concept of aromaticity accounts for the extraordinary thermodynamic stability of a number of charged and neutral cyclic π-conjugated organic systems. Equally, antiaromaticity has accounted for the instability of a number of these systems with $4n$ π electrons. The concept of aromatic character was extended to include homoaromaticity in order to account for the high stability of molecules in which conjugation is interrupted in one or more places by aliphatic groups.[1] This concept of homoaromaticity