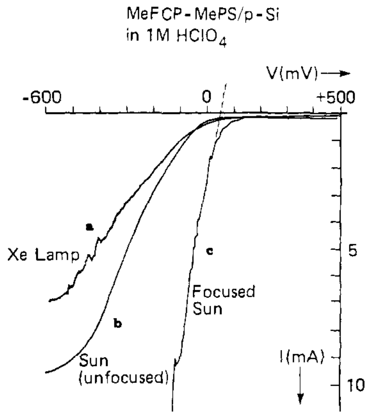

Figure 2. Current/voltage plots (vs. SCE) of an irradiated MeFCP–MePS modified p-Si photocathode (Pt anode, scan rate 50 mV/s). The illumination conditions are only qualitatively defined: (a) a Xe are lamp, (b) diffuse sunlight, and (c) sunlight focused through a magnifying glass.

of hydrogen liberation at a Pt electrode in HBF_3OH containing FCP occurs at −100 mV vs. SCE; at an irradiated p-type silicon cathode,[14] hydrogen is produced at +200 mV vs. SCE; a gain of 300 mV.

A much more efficient way of using FCP as a hydrogen generation catalyst in a liquid junction solar cell would be to cover the photocathode surface with a FCP containing polymer, which not only achieves very high concentrations of FCP at the surface but also provides the very desirable protection of the electrode against attack by the electrolyte. To prepare such a polymer bound FCP, we made use of our recent finding that FCP and its bridge-methylated derivatives 1-MeFCP (**3**) and 1,12-Me_2FCP can be cleanly deprotonated to produce bridge carbanions.[10] Reaction of the carbanion of **3** with commercial poly(chloromethyl)styrene) produced polymer-bound 1-MeFCP.[16] A solution of this methylferrocenophane–(methylpolystyrene) polymer ("MeFCP–MePS") in THF was used to deposit a film of polymer on either the ⟨100⟩ or ⟨111⟩ face of p-type silicon electrodes. With 870 mW/cm^2 Xe light, a MeFCP–MePS-modified p-type silicon electrode (resistivity 1 Ω cm, ⟨111⟩ face exposed) of 0.16-cm^2 area operated with a maximum underpotential of 450 mV (Figure 1), where "underpotential" refers to the difference in potential between this electrode and a shiny platinum electrode at equal currents under these conditions.[17] At 31.0 mA and −540 mV (the point marked in Figure 1), the underpotential was 400 mV. At more negative potentials, a saturation current of 37 mA was reached. The electrode maintained this excellent performance throughout 5 days.

We were concerned that the low metal basicity of the ferrocenophanes would restrict us to HBF_3OH as the electrolyte, but we subsequently found that hydrogen evolution occurs readily and at underpotentials of 250–350 mV on illuminated MeFCP–MePS-modified p-type silicon electrodes even in dilute acid media such as 1 M $HClO_4$, 1 M HBF_4, and 1 M HCl. Irradiating a MeFCP–MePS-coated p-Si electrode by a Xe arc lamp or by sunlight in a cell containing 1 M $HClO_4$ as the electrolyte lead to rapid hydrogen evolution at potentials negative of 0 mV vs. SCE, corresponding to an underpotential of approximately 250 mV compared to the standard potential of hydrogen. Simply focusing the sunlight onto the electrode through a magnifying glass held in front of the cell increased the underpotential to 300 mV and, as expected, led to a much steeper rise in current. These results are shown in Figure 2.

If the same mechanism of double protonation and hydrogen elimination applies for FCP in solution and in surface-confined FCP, we need to explain why we see this hydrogen evolution from dilute acids although we know that only the strongest acids can protonated metallocenes. The concentration of FCP in the surface layer at the photocathode is several orders of magnitude higher in the MeFCP–MePS film (approximately 2 M) than in the experiments with FCP in solution (around 10^{-3} M). We thus may simply be looking at the effect of concentration on a continuously shifting equilibrium, which depends on the FCP concentration and the square of the proton concentration. Using dilute acids, this equilibrium will be largely on the side of the nonprotonated FCP unless its concentration is increased dramatically—as we are doing in the case of MeFCP–MePS.

The above results demonstrate the usefulness of ferrocenophane derivatives in photoelectrochemical hydrogen generation. We are currently exploring structurally related materials[19,20] and binuclear compounds of higher metal basicity.

Acknowledgment. Eda Easton deserves our gratitude for advice on the right choice of wax and for donating some of her casting wax. We acknowledge many discussions with Drs. Gordon (San Jose) and Rusling (Storrs) concerning the electrochemical aspects of this work.

Registry No. 1, 1294-39-9; HBF_3OH, 16903-52-9; $HClO_4$, 7601-90-3; Si, 7440-21-3.

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[14] Our cathodes are boron-doped p-type silicon (ρ = 1–10 Ωcm, ⟨100⟩ or ⟨111⟩ face exposed) with 5000 Å Al sintered on the back. The flattened end of a copper lead was attached to the back with silver epoxy; the wire was covered with Teflon tubing (1 mm inner diameter). The back and the sides of the electrode were covered with wax.

[15] The commerical poly((chloromethyl)styrene) (poly(vinylbenzyl chloride), Aldrich) is a 60/40 mixture of ortho and para isomers.

[16] Elemental analysis of the resulting polymer-bound FCP (calculated for a 1:1 MeFCP–poly(methylstyrene) ($C_{32}H_{31}Fe_2$): C, 72.89; H, 5.93; Fe, 21.18%. Found: C, 67.87; H, 5.50; Fe, 19.20; Cl, 1.80%) shows that some of the chloromethyl groups still are present (1.8% chlorine remains), but approximately 75% of the reactive polymer sites now carry a MeFCP group.

[17] This cell does not represent an independent solar energy device, because we are supplying an external potential in addition to the light-generated one. The amount of external energy needed for a given process is reduced by the energy converted by the photocathode. To assign a conversion efficiency to this light-to-chemical-energy process is without much merit. In related work[18] on InP photocathodes, a "net power density gain" of 12% was defined. Using the same approach, our Si cathode has a gain of 9%. This number is given for calibration purposes only. The same authors also referred to the term "underpotential" which we use here.

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Pulse Radiolysis Generation of Sulfur Radical Cations Stabilized by Neighboring Carboxylate and Alcohol Groups

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Radical cations derived from dialkyl thioethers are transient species that undergo diverse reactions.[1-3] Their stability and ease of formation are dramatically enhanced by electron-rich neighboring groups with favorable geometries which facilitate sulfur–sulfur or sulfur–heteroatom p-orbital overlap.[4] Since such sulfur-centered radicals have recently gained prominence as possible

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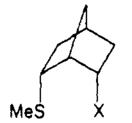
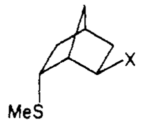
intermediates in redox reactions of biomolecules, e.g., intermediate ES formed by oxidation of yeast cytochrome *c* peroxidase,[5] it is essential to characterize analogous model systems where physical and chemical properties can be unambiguously determined. This paper reports the pulse radiolytic generation of $(RR^1SOR^2)\cdot$ radicals in systems whose molecular architecture favors their formation and increases their stability.

Neighboring carboxylate and alcohol groups were shown by electrochemical techniques to facilitate oxidation of the sulfides **1a**,**b**.[6] Electrochemical oxidation of these compounds leads to an irreversible two-electron process thereby precluding observation of the one-electron intermediate. However, hydroxyl radical induced oxidation makes such studies feasible.

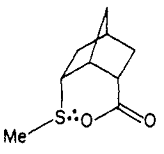


1a, $X = CO_2^-$
b, $X = CH_2OH$
c, $X = C(CH_3)_2OH$

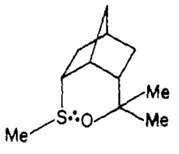


2a, $X = CO_2^-$
b, $X = CH_2OH$
c, $X = C(CH_3)_2OH$

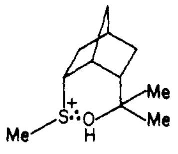
Pulse radiolysis of 10^{-4} M *endo*-**1a** and *exo*-carboxylate **2a** in N_2O-saturated aqueous solutions provided several transient species. Short-lived adduct radicals of the ·OH and sulfur atom with $t_{1/2} < 1$ μs and λ_{max} around 360 nm and long-lived α-(alkylthio)alkyl radicals with λ_{max} around 280 nm can unambiguously be assigned on the basis of previous studies of aliphatic sulfides.[2] In addition, a new transient absorption with a maximum at 390 nm is observable for the *endo*-carboxylate **1a**. This species exhibits an exponential decay with $t_{1/2} \approx 30$, 60, and 50 μs at pH 3, 7, and 10, respectively.[7] No such absorption is observed for the corresponding *exo*-carboxylate **2a**. The unique 390-nm transient from the endo compound is assigned structure **3a**, which possesses a $\sigma^2\sigma^{*1}$ three-electron bond between sulfur and oxygen. This assignment is based on the general observation that the unpaired p-electron in $R_2S^{+}\cdot$ shows a strong tendency for stabilization by a nonbonding p-electron pair of a second heteroatom and that the optical absorption of such species is attributable to a $\sigma \rightarrow \sigma^*$ transition[4] to a first approximation. An alternative bonding scheme for **3a** is approximately described as a three-center, three-electron bond. Such a bonding scheme has been suggested for a related radical.[8] The overall uncharged character of this new species has been further established by time-resolved conductivity measurements carried out simultaneously with the optical monitoring.



3a



3b



4

Radical cations with the functional groups $(>S\therefore S<)^+$ typically absorb in the 460–500-nm range. Such species formed by the reaction of $R_2S^{+}\cdot$ with the sulfur atom of a second molecule have not been observed in these studies. This is as expected because of the low solute concentrations.

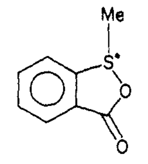
Pulse radiolysis of *endo*-**1b** and 1° *exo*-alcohol **2b** in N_2O-saturated solutions at pH 8.5, respectively, both resulted only in the formation of the short-lived ($t_{1/2} < 1$ μs) ·OH adduct radical and the α-(alkylthio)alkyl-type radical derived by deprotonation of $R_2S^{+}\cdot$. These radicals exhibit comparable half-lives and absorption spectra as the corresponding radicals obtained from **1a** and **2a**, which are described above, and to those obtained from simple aliphatic sulfides reported previously. Thus it appears that a stable two-center, three-electron or three-center, three-electron radical species is not formed in the oxidation of this primary alcohol.

The corresponding ·OH adducts and α-(alkylthio)alkyl radicals are also formed from the tertiary alcohols **1c** and **2c**. However, oxidation of the tertiary *endo*-alcohol **1c** led, again, to a longer lived transient absorption in the 400-nm range. In solutions of pH 4 a maximum is observed at 420 nm, which decays exponentially with a half-life of ca. 30 μs. Conductivity experiments revealed that the absorbing species is positively charged. Similar experiments at pH 8 showed a shift in λ_{max} to 400 nm, a half-life of ca. 200 μs, and the overall neutral nature of the transient. Therefore, as with radical **3a** we assign structures with an SO bond, such as the three-electron bonded structures **3b** and **4**, to the respective transient at pH 4 and 8, which are related by an acid–base equilibrium. The results mean that radical **3b** is a relatively strong base.

$$\mathbf{4} \rightleftarrows \mathbf{3b} + H^+$$

The stabilization of the bond between the sulfur atom and neighboring oxygen atom in the oxidized tertiary alcohol is likely to be facilitated by the two bulky methyl groups in **1c**/**3b** and **4**, which will force the alcohol group toward the sulfur atom.[9] In the primary alcohol **1b**, on the other hand, the alcohol group points away from the methylthio group in the lowest energy conformer[10] thus precluding sulfur–oxygen interaction. In case of the *endo*-carboxylate (**1a**/**3a**) this consideration is of course irrelevant since both oxygen atoms are equivalent.

The present results are in excellent agreement with the general observation that favorable steric arrangements enhance the neighboring group participation and the stability of σ^2,σ^{*1} three-electron bonds, particularly in systems where two atoms of quite different electronegativity are to interact. Further studies on the nature of the bonding in radicals **3a**,**b** and **4** are under way. Our experiments therefore provide a model for redox proteins containing sulfide and neighboring nucleophilic oxygen functions. Our species may be compared with radicals **5** and **6**, studied by Perkins et al.[8] and Gara et al.,[11,12] respectively, by means of ESR. However, our results are the first measurements on such radicals derived from sulfides that carry only alkyl groups with alkoxy and acyloxy substituents in solution.



5

$Me_2\dot{S}OSiMe_3$

6

Note Added in Proof. After this paper was submitted for publication, we received a preprint of a paper authored by C. Chatgilialoglu, A. L. Castelhano, and D. Griller, in which they report the absorption spectrum of **5**. This radical shows a λ_{max} between 380 and 390 nm in dichloromethane at 238 K.

Acknowledgment. The support given for this work by the Deutsche Forschungsgemeinschaft (DFG) and the National Institutes of Health (HL15104) is gratefully acknowledged. We thank Dale Swanson for determining the pK_a of *endo*-acid **1a**, $X = CO_2H$.

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(7) It is interesting to note that the yield of radical **3a** from **1a** is independent of pH from 3–10 if ·OH radicals are used as oxidant. Since the pK_a of *endo*-acid **1a**, $X = CO_2H$ is 5.5 and the half-life of radical **3a** varies only by a factor of 2 in the pH range 3–10, both *endo*-acid **1a**, $X = CO_2H$ and *endo*-carboxylate **1a** yield radical **3a** with comparable rates. The mechanisms by which each of these species forms radical **3a** is under further study.

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