lecular ions measured experimentally were M (43), M +2 (6), and M + 4 (51). Considering that a portion of the 11-hydroxyl group is derived from dioxygen, this result clearly indicates that the transfer of the hydroperoxy oxygen to carbon 11 of II is intramolecular.

These findings indicate that hematin catalyzes the cyclization of the internal peroxide oxygen to the 11,12-double bond and the transfer of the terminal peroxide oxygen to carbons 9 or 11. A mechanistic hypothesis consistent with the experimental observations is outlined in Scheme I. Hematin reduces the hydroperoxide by one electron generating a fatty acid alkoxyl radical and a ferryl-hydroxo complex.[10] The alkoxyl radical cyclizes to an epoxide-containing allylic radical.[11] The epoxy allylic radical can couple at either of the allylic termini with the hydroxyl radical coordinated to hematin or to dioxygen following diffusion from the solvent cage. The reciprocal relationship between the incorporation of hydroperoxide or molecular oxygen at carbons 9 or 11 suggests that the ferryl-hydroxo complex and dioxygen compete for the trapping of the same intermediate, the epoxy allylic radical.[12] The higher percentage of peroxy oxygen trapping at carbon 11 is most likely due to the proximity of this allylic terminus to the ferryl-hydroxo complex.

Oxygen rebounds have been observed in the peroxide-dependent and iodosylbenzene-dependent hydroxylations of alkanes catalyzed by ferrous ion and metalloporphyrins, respectively.[13] In both cases, the metal center reduces the oxidizing agent by two electrons and forms an oxo complex that transfers oxygen to the alkane. Oxygen rebounds have not been observed in peroxide-dependent oxidations catalyzed by iron porphyrins presumably because of the propensity of the catalyst to reduce peroxide by one electron in the initial step of oxidation.[14] Our finding that hematin catalyzes the rearrangement of I to epoxy alcohols via an oxygen rebound derives from the fact that the initial peroxide reduction product, an alkoxyl radical, can cyclize to generate a carbon-centered radical capable of coupling to the hydroxyl radical coordinated to iron. The 11,12-double bond of I thus serves as an intramolecular trap that transforms the initial peroxide reduction product into a derivative capable of participating in an oxygen rebound. The coupling reaction may be aided by the fact that the radical pair is generated in a solvent cage provided by detergent micelles.[15] Recent work has shown that micelles limit the diffusion of geminate radicals to an extent that suggests the microenvironment of a radical pair in a micelle acts as a "supercage" relative to that in homogeneous solution.[16] This can result in the prolongation of the lifetime of the solvent cage by factors of up to 10^4.[16a] This would not only enhance the probability that the epoxy allylic radical would couple to the hydroxyl group but also increase the cyclization of the initial alkoxyl radical to the epoxy allylic radical prior to diffusive separation of the initial radical pair.

This report demonstrates that simple heme complexes, in the absence of protein, can catalyze the rearrangement of unsaturated fatty acid hydroperoxides to epoxy alcohols in a reaction that appears mechanistically related to that observed in mammalian tissues. Since the activity in rat lung cytosol that catalyzes this reaction is not abolished by heating and does not chromatograph in a discrete zone, it has been suggested that it is not due to an enzyme.[4] Our results suggest that free heme present in lung extracts may play a role in epoxy alcohol formation in such in vitro experiments.

Acknowledgment. We are grateful to John Groves for helpful discussions. Harold Gardner kindly provided a sample of epoxy alcohol II for chromatographic comparison. Mass spectra were obtained at the Michigan State University Regional Mass Spectrometry Facility with the aid of Betty Baltzer. This work was supported by a research grant from the National Institutes of Health (GM 23642). L.J.M. is a recipient of an American Cancer Society Faculty Research Award (FRA 243).

(10) The interaction of hydroperoxides with hematin is complex. Investigators have proposed that hematin reduces hydroperoxides by one electron or two electrons or oxidizes them by one electron: (a) Portsmouth, D.; Beal, E. A. *Eur. J. Biochem.* **1971**, *19*, 479-487. (b) Jones, P.; Mantle, D.; Davies, D. M.; Kelley, H. C. *Biochemistry* **1977**, *16*, 3974-3978. (c) Kalyanaraman, B.; Mottley, C.; Mason, R. P. *J. Biol. Chem.* **1983**, *258*, 3855-3858. Our data strongly suggest that under the conditions described hematin reduces fatty acid hydroperoxides by one electron.

(11) (a) Gardner, H. W. *J. Agric. Food Chem.* **1975**, *23*, 129-136. (b) Gardner, H. W.; Weisleder, D. W.; Kleiman, R. *Lipids* **1978**, *13*, 246-252. (c) Gardner, H. W.; Kleiman, R. *Biochim. Biophys. Acta* **1981**, *665*, 113-125.

(12) If the epoxyols that incorporate O_2 at carbons 9 and 11 arise via a separate intermediate than those that retain both peroxide oxygens, the incorporation of O_2 at both carbons should be equivalent.

(13) (a) Groves, J. T.; McClusky, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 859-861. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *Ibid.* **1979**, *101*, 1032-1033. (c) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413-3415.

(14) (a) Groves, J. T. In "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980; p 125-162. (b) Oxygen rebound has been reported in the enzymatic decarboxylation of peroxyphenylacetic acid to benzyl alcohol catalyzed by cytochrome P-450. White, R. E.; Sligar, S. G.; Coon, M. J. *J. Biol. Chem.* **1980**, *255*, 11108-11111. One-electron reduction of the peroxide was proposed as the first step in the reaction.

(15) The reaction undoubtedly occurs in detergent micelles. Hematin exists in buffered aqueous solution as a dimer that possesses very low peroxidase activity: (a) Brown S. B.; Dean, T. C.; Jones, P. *Biochem. J.* **1970**, *117*, 733-739. (b) Jones, P.; Robson, T.; Brown, S. *Ibid.* **1973**, *135*, 353-359. Addition of Tween 20 at the concentrations indicated induces a dramatic bathochromic shift of the Soret band from the broad, poorly defined structural absorption of the dimer to the sharp much more intense absorption of the monomer dissolved in an organic solvent. The system can, therefore, be considered to contain hematin in equilibrium between aqueous and micellar compartments. Only hematin dissolved in the micellar compartment is catalytically active.

(16) (a) Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431-7432. (b) Turro, N. J.; Weed, G. C. *Ibid.* **1983**, *105*, 1861-1868.

Integrated Chemical Systems: Photocatalysis at Semiconductors Incorporated into Polymer (Nafion)/Mediator Systems

M. Krishnan, James R. White, Marye Anne Fox,* and Allen J. Bard*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received August 11, 1983

The utilization of semiconductors for photoelectrochemical and photocatalytic processes in which light is used to drive chemical reactions often requires the construction of integrated chemical systems.[1] These are designed heterogeneous systems consisting of several components acting in a synergistic way to carry out a particular process. For example, the photogeneration of hydrogen on p-type semiconductor electrodes (e.g., GaAs and Si) is enhanced by the addition to its surface of a viologen-bearing polymer layer containing platinum.[2] A number of studies on the utilization of semiconductor particles (e.g., TiO_2, CdS), frequently treated with appropriate catalysts to carry out photocatalytic and photosynthetic processes, have been described.[3] In these systems irradiation of suspensions or colloidal dispersions of the semiconductors in solutions of suitable redox couples (relays) and other reagents produces electron/hole pairs which drive oxidations and reductions

(1) Bard, A. J.; Fan, F. R.; Hope, G. A.; Keil, R. G. *ACS Symp. Ser.* **1983**, *No. 211*, 93.

(2) (a) Abruna, H. D.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 6898. (b) Dominey, R. N.; Lewis, N. S.; Bruce, J. A.; Bookbinder, D. C.; Wrighton, M. S. *Ibid.* **1982**, *104*, 467.

(3) See, for example: (a) Frank, S. N.; Bard, A. J. *J. Phys. Chem.* **1977**, *81*, 1484. (b) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 5985. (c) Kalyanasundaram, K.; Borgarello, E.; Gratzel, M. *Helv. Chim. Acta* **1981**, *64*, 362. (d) Thewissen, D. H. M. W.; Tinnemans, A. H. A.; Eeuwhorst-Reinten, M.; Timmer, K.; Mackor, A. *Nouv. J. Chim.* **1983**, *7*, 191.

0002-7863/83/1505-7002$01.50/0

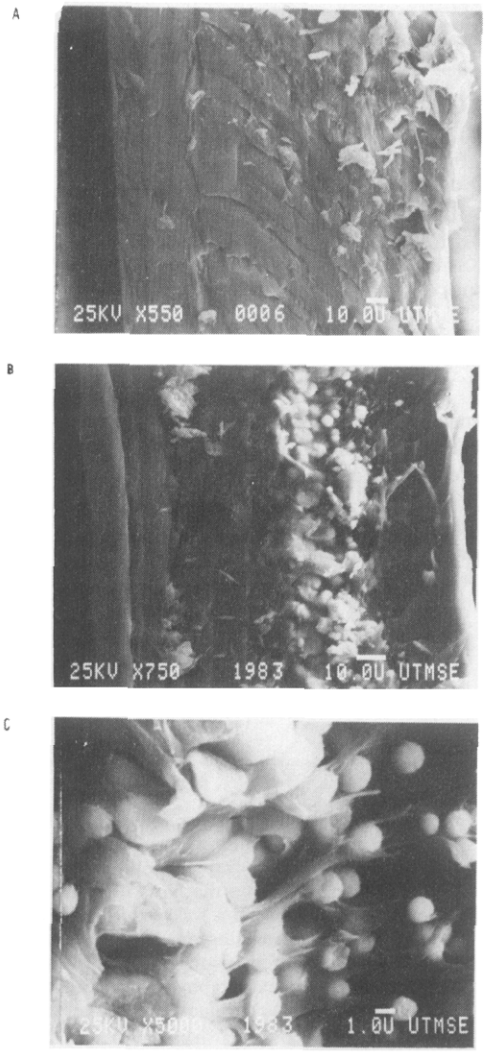

Figure 1. Scanning electron micrographs showing cross-sectional views of Nafion membrane: (A) Nafion (×550), (B) Nafion loaded with CdS (×750), (C) detail, as in (B), (×5000). Calibrating bars are 10.0, 10.0, and 1.0 μm, respectively.

at the particle surfaces. While these particulate systems have been useful in a number of reactions, they are not convenient in continuous-flow or recirculation arrangements nor for the incorporation of sensitizers and/or relays on or near the semiconductor surface. We describe here a method of incorporation of a dispersed semiconductor throughout an ionically conductive polymer membrane, in which suitable relays and catalysts can also be added to promote photocatalytic reactions on these membranes. To our knowledge the only previous system involving a dispersed semiconductor/polymer arrangement was that of Meissner et al.[4] In that system, monograin CdS particles on the order of 40-μm diameter were physically embedded in a thin, nonconducting polyurethane membrane and various photoprocesses examined. The technique we describe offers better control of the particle size and distribution and the advantage of an ion-conductive membrane.

Consider the incorporation of CdS into Nafion. A Nafion membrane (type 125, 1100 equiv wt; thickness ~0.13 mm) was pretreated by boiling in concentrated HNO_3 and was subsequently immersed in a 1.0 M solution of Cd^{2+} (pH 1) to incorporate Cd^{2+} in the membrane by ion exchange. Exposure of this membrane to H_2S produces CdS and the clear membrane becomes bright yellow and opaque. Scanning electron microscopy (SEM) of membranes formed in this way show CdS deposits on or near the surface of the membrane leaving the bulk of the membrane void of deposits. Alternatively, the Nafion can be positioned as a separator between solutions of Cd^{2+} and H_2S for production of CdS within the membrane. Figure 1B is a SEM photograph showing a cross-sectional view of CdS deposits, which are formed well inside the Nafion membrane; a naked Nafion membrane for comparison is given in Figure 1A. The CdS precipitates as spherical particles of a diameter 1 μm or smaller, which can then agglomerate into larger deposits (Figure 1C). After CdS is produced, the cation exchange sites in the polymer are again available, and a cationic relay, such as methylviologen (4,4'-dimethylbipyridinium or MV^{2+}), can be incorporated into the membrane. If this membrane is now immersed in a 1.0 M NaOH solution containing 0.1 M tartaric acid (as a sacrificial donor[6]) and irradiated with a 1600-W xenon lamp with appropriate filters, the membrane quickly turns violet; photogenerated electrons cause reduction of MV^{2+} to $MV^{+}\cdot$ and the holes oxidize tartaric acid. When 1.0 mM MV^{2+} is added to the solution, electron transfer from the membrane MV^{+} and/or the irradiated CdS also causes $MV^{+}\cdot$ formation in the solution. The rate of $MV^{+}\cdot$ formation in solution can be compared with that of an irradiated colloidal dispersion under similar conditions by continuous Coulometric oxidation of the $MV^{+}\cdot$ produced at a large-area Pt electrode.[6] In this case the Nafion/CdS/MV^{2+} system produces a current of 0.1 mA compared to 4.0 mA produced by a colloidal CdS dispersion.[7]

We have also found that platinum can be incorporated into this CdS/MV^{2+} membrane system. By analogous techniques, incorporation of other semiconductors, such as TiO_2 and ZnS, also appears possible. Details of these results will be given in future publications.

Acknowledgment. This research was supported by a contract from the Gas Research Institute (No. 5082-260-0756).

(4) Meissner, D.; Memming, R.; Kastening, B. *Chem. Phys. Lett.* **1983**, *96*, 34.

(5) Grot, W. *Chem. Ing. Tech.* **1978**, *50*, 299.

(6) White, J.; Bard, A. J., unpublished results.

(7) The currents were obtained with 1-cm^2 geometrical area of Nafion/CdS, which was typically loaded with 3 mg/cm^2 of CdS. This is compared to currents obtained from 10 mg of dispersed CdS powder (Aldrich 99.99%). The solution volume in each case was 40 mL.