Acknowledgment. This work was supported by the following grants: NIH GM17880 and NSF MPS70-01722-A03. We are indebted to discussions with H. Taube.

References and Notes

(1) (a) I. C. Gunsalus, J. R. Meeks, J. D. Lipscomb, P. Debrunner, and E. Munck in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1974, p 561; (b) V. Ullrich, *Angew. Chem., Int. Ed. Engl.*, **11**, 701 (1972).

(2) (a) J. P. Collman, T. N. Sorrell, and B. M. Hoffman, *J. Am. Chem. Soc.*, **97**, 913 (1975); (b) J. P. Collman, T. N. Sorrell, and K. O. Hodgson, *ibid.*, submitted for publication; (c) S. Koch, S. C. Tang, R. H. Holm, and R. B. Frankel, *ibid.*, **97**, 914 (1975); (d) S. Koch, S. C. Tang, R. H. Holm, R. B. Frankel, and J. A. Ibers, *ibid.*, **97**, 916 (1975).

(3) J. O. Stern and J. Peisach, *J. Biol. Chem.*, **249**, 7495 (1974).

(4) The following abbreviations are used: DMSO = dimethyl sulfoxide, THF = tetrahydrofuran, THT = tetrahydrothiophene, N-MeIm = *N*-methylimidazole, (Na)SCH$_3$ = sodium mercaptide dibenzo-18-crown-6 complex, TPP = tetraphenylporphyrin dianion, TpivPP = $\alpha,\alpha,\alpha,\alpha$-tetra-(*o*-pivalamidophenyl)porphyrin dianion,[5] PPIXDEE = protoporphyrin IX diethyl ester dianion.

(5) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).

(6) There are some notable discrepancies between this work and that of Stern and Peisach.[3] For example, in DMSO, they report a peak at 450 nm for the mercaptide species, whereas we find the analogous absorption at 462 nm. For the mercaptan species, they report a peak at 413 nm, whereas we observe a band at 422 nm. It is possible that these differences arise from the fact that they used protoporphyrin IX while we employed the diethyl ester. It is interesting to note that the ratio A_{450}/A_{555} = 4 for the previous work, whereas for most cytochrome P$_{450}$'s this ratio is closer to 10.

(7) Undoubtedly the protein environment plays a role in the exact position of the 450 peak. Recall that the picket fence porphyrin,[5] TpivPP, has four amides on one side of the porphyrin ring and PPIXDEE has two polar ester groups.

(8) Presumably, the air serves to oxidize the ferrous complex to ferric. Excess mercaptide is then necessary to reduce the iron back to the ferrous state. We noted previously[2a] the propensity of ferric mercaptide complexes to reduce spontaneously giving Fe(II) species.

(9) We have already noted[5] that *meso*-tetraarylporphyrins often have different absorption spectra so that it is not unusual that extinction coefficients for FeTpivPP are different from those of the natural system.

(10) This supposition has strong support in the yet unpublished work of Taube and Kuehn comparing stability constants for mercaptide and mercaptan binding to ruthenium(II) and -(III).

James P. Collman,* Thomas N. Sorrell
Department of Chemistry, Stanford University
Stanford, California 94305

Received April 18, 1975

Evidence for the Oxidation of Supersensitizers during Photoelectrochemical Supersensitization at the CdS Electrode

Sir:

Studies on spectral sensitization have recently been carried out by a number of authors using electrochemical procedures,[1-5] principally with the aim of elucidating the mechanism of spectral sensitization. The experimental results reported in the literature can on the whole be interpreted by postulating the electron transfer mechanism (the electron transfer from excited dyes to a semiconductor), which has extensively been discussed in photographic science. Provided that the spectral sensitization at n-type semiconductor electrodes involves the electron transfer mechanism, sensitizing dyes or supersensitizers (reducing agents) should, at least momentarily, be oxidized. However, the detection of oxidized forms of sensitizers or supersensitizers has not thus far been reported.

In the present study we demonstrated the oxidation of supersensitizers in the course of spectral sensitization at the CdS electrode, by means of a rotating ring-disk electrode (RRDE) system, where a CdS single crystal served as the disk electrode and Au as the ring electrode.

The CdS single crystal employed was an n-type semiconductor, with a carrier density of 7.4×10^{16} cm^{-3}. The electrode was a pellet having an average radius of 3.25 mm and a thickness of 1.0 mm. In order to ensure an ohmic contact with a lead wire, indium was vacuum-evaporated onto a small part of the electrode surface. The CdS electrode was mounted in a Teflon rod, together with a gold ring electrode, as illustrated in Figure 1.

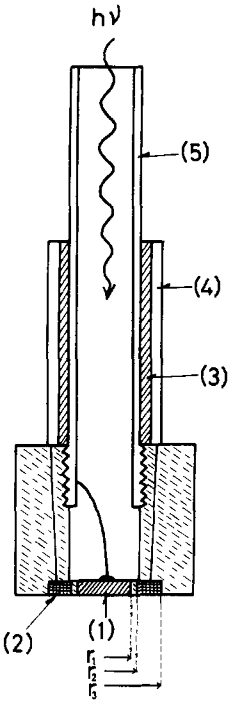

Figure 1. Ring-disk electrode assembly: (1) CdS single crystal (disk electrode); (2) Au (ring electrode); (3) insulator; (4), (5) brass cylinders, r_1 = 3.25 mm, r_2 = 3.75 mm, r_3 = 5.0 mm.

Rhodamine B and 1,1′-diethyl-2,2′-quinocyanine were used as sensitizing dyes. As supersensitizers, hydroquinone and potassium ferrocyanide were employed. The electrolyte was a 0.2 *M* Na$_2$SO$_4$ solution. All the chemicals used were of reagent grade.

A rotating ring-disk electrode system Type RRDE-1 and a dual potentiogalvanostat Type DPG-1 (Nikko Keisoku Co.) were used for the measurements.

The light source was a 500-W xenon lamp, and the wavelength of the illuminating light was selected with the use of a monochromator or colored glass filters. The illumination of the CdS electrode–electrolyte interface was transmitted through the bulk of the CdS electrode.

In the absence of sensitizing dyes in the electrolyte solution, only a small photocurrent can be observed with the illumination of light in the wavelength range above 540 nm, since the forbidden band width of CdS is about 2.4 eV. When rhodamine B was added into the electrolyte solution, a disk photocurrent, whose spectral distribution is quite close to the absorption spectrum of the dye adsorbed on CdS, was obtained as shown in Figure 2. In this case, no reduction current at the Au ring electrode was observed. This fact presumably suggests that the oxidation product of rhodamine B in the course of the sensitization process is of quite irreversible nature or is extremely unstable.

When hydroquinone was added to the dye-containing electrolyte solution, the photocurrent in the region of dye absorption was remarkably enhanced (supersensitization) as shown in Figure 2. When the potential of the Au ring electrode was fixed at, e.g., −0.4 V vs SCE, a reduction current, which was approximately proportional to the sensitization current at the CdS disk electrode, was detected at the ring electrode (broken curve in Figure 2).

In order to identify the species undergoing reduction at the ring electrode, the current–potential characteristic of

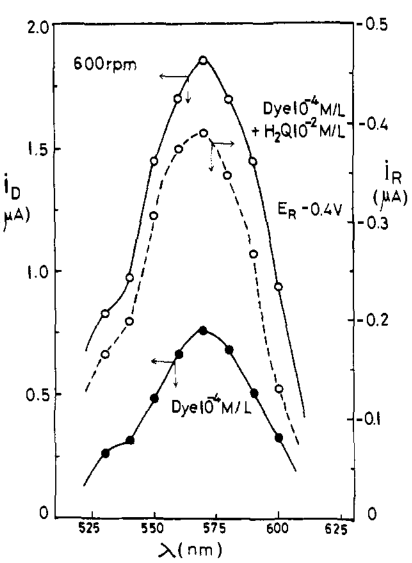

Figure 2. Currents observed at the CdS disk and Au ring electrodes during spectral sensitization with rhodamine B and supersensitization with hydroquinone: i_D, disk current; i_R, ring current; —●—, disk current with 10^{-4} M of rhodamine B; ○ (solid line), disk current with 10^{-4} M of rhodamine B + 10^{-2} M of hydroquinone; ○ (dashed line), ring current with 10^{-4} M of rhodamine B + 10^{-2} M of hydroquinone.

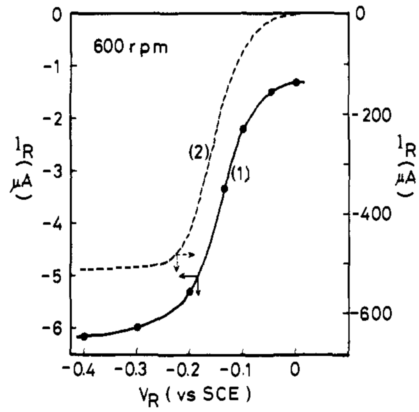

Figure 3. Current-potential characteristics for (1) the ring electrode under supersensitization on CdS disk (10^{-4} M of rhodamine B + 10^{-2} M of hydroquinone) and (2) the Au ring electrode (10^{-3} M of quinone).

the ring electrode where the supersensitization reaction occurred on the CdS disk electrode was compared with that of the Au ring electrode where only quinone was present in the solution. The two current-potential curves coincide fairly well, as depicted in Figure 3. From these observations we conclude that hydroquinone is oxidized to quinone in the course of supersensitization.

We measured the collection efficiency ($-i_R/i_D$) for the CdS disk-Au ring system as a function of the rotation rate in the range 200-1000 rpm. Both disk photocurrent under the illumination with the constant intensity and ring reduction current were steady state quantities and independent on the rotation rate. Therefore, no appreciable change of the collection efficiency was observed. According to the theory of the RRDE system,[6] the collection efficiency for this rotation rate region is expected to decrease as the rotation rate increases, provided that the rate of the first-order reaction between hydroquinone and the supposed oxidized species of rhodamine B is the range of 10^{-2} to 2×10^2 sec^{-1}. The present result indicates that the reaction rate is much greater than 10^2 sec^{-1}.

When 1,1′-diethyl-2,2′-quinocyanine was used as the sensitizing dye, just as in the case of rhodamine B, the reduction of quinone was detected at the Au ring electrode. Furthermore, when potassium ferrocyanide was added to the dye-containing electrolyte solution, reduction of ferricyanide ion was detected at the ring electrode.

Based upon the results of the present study, we conclude that reducing agents undergo oxidation in the course of photoelectrochemical supersensitization at the CdS single-crystal electrode.

References and Notes

(1) H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **72**, 437 (1968).
(2) K. Hauffe, H. J. Danzmann, H. Pusch, J. Range, and H. Volz, *J. Electrochem. Soc.*, **117**, 993 (1970).
(3) A. Fujishima, E. Hayashitani, and K. Honda, *Seisan Kenkyu*, **23**, 31 (1971).
(4) A. Fujishima, E. Hayashitani, and K. Honda, *Seisan Kenkyu*, **23**, 363 (1971).
(5) A. Fujishima, T. Watanabe, O. Tatsuoki, and K. Honda, *Chem. Lett.*, 13 (1975).
(6) W. J. Albery and S. Bruckenstein, *Trans. Faraday Soc.*, **62**, 1946 (1966).

Akira Fujishima,* Takashi Iwase
Faculty of Technology, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama, Japan

Tadashi Watanabe, Kenichi Honda
Institute of Industrial Science, University of Tokyo
Roppongi, Minato-ku, Tokyo, Japan

Received January 28, 1975

Formation of Ruthenium(II) Nitrile Complexes by Reaction of Hexaammineruthenium(III) with Aldehydes

Sir:

Recent reports have shown that under alkaline conditions coordinated ligands may effect nucleophilic attack at carbonyl centers in organic compounds.[1-4] For example, reactions of Co(III) and Pt(IV) ammines with ketones yield the corresponding Co(III) and Pt(IV) imine complexes.[5a] A similar reaction between hexaammineruthenium(III) and diones produces the corresponding Ru(II) diimine.[5a]

We now wish to report the formation of nitrilepentaammineruthenium(II) complexes, $(H_2N)_5Ru{\cdot}NCR^{2+}$ (R = $-CH_3$ or $-C_6H_5$), in the reaction of hexaammineruthenium(III), $Ru(NH_3)_6{}^{3+}$, with the appropriate aldehydes. This appears to be the first report of the formation of a nitrile from the reaction of an aldehyde with a transition metal ammine nucleophile.[5b]

A pK_a of approximately 12.4 has been reported[6] for the $Ru(NH_3)_6{}^{3+}$ ion, suggesting almost complete deprotonation in 1 M OH^-. Solutions of approximately 0.03 M $[Ru(NH_3)_6]Br_3$ containing a 100-fold excess of acetaldehyde or benzaldehyde react rapidly (complete in less than 1 min based on color change) to produce the nitrile complexes; addition of aqueous $NaClO_4$ precipitates the solid products. The isolated solids show infrared bands in the 2200-cm^{-1} ($\nu_{C\equiv N}$) region of the spectrum as well as bands characteristic of Ru(II) ammines in the 1300-cm^{-1} region.[7] The ultraviolet-visible and infrared spectra of the products are in good agreement with those reported in the literature[8] for the pentaammineruthenium(II) complexes of benzo- and acetonitrile prepared by the direct action of the respective nitriles on $Ru(NH_3)_5H_2O^{2+}$.

The overall reaction may be represented by the equation

$$(H_3N)_5Ru^{III}NH_3{}^{3+} + 2OH^- + RCHO + X \rightarrow (H_3N)_5Ru^{II}NCR^{2+} + 3H_2O + X^-$$