

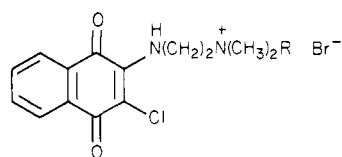
# Mediated Electrochemical Reduction of Oxygen to Hydrogen Peroxide via a Surface-Confined Naphthoquinone Reagent and the Mediated Electrochemical Reduction of a Naphthoquinone Redox Reagent Anchored to High Surface Area Oxides

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**Abstract:** Derivatives of 1,4-naphthoquinone, 2-chloro-3-[[2-(dimethylpropylammonio)ethyl]amino]-1,4-naphthoquinone bromide, Ia, and 2-chloro-3-[[2-(dimethyl(3-(trimethoxysilyl)propyl)ammonio)ethyl]amino]-1,4-naphthoquinone bromide, Ib, have been synthesized and used as solution and surface-bound catalysts, respectively, for the electrochemical and photoelectrochemical reduction of  $O_2$  to  $H_2O_2$ . The surface derivatizing reagent Ib having the  $-Si(OCH_3)_3$  functionality can be used to functionalize a variety of surfaces including electrode (Pt, W, p- $WS_2$ ) materials and high surface area oxides ( $SiO_2$ ,  $Al_2O_3$ ). The surface reagent,  $[Q/QH_2]_{surf}$ , has the same  $E^\circ$  as Ia in solution,  $\sim -0.4$  V vs. SCE at pH 7. The  $[QH_2]_{surf}$  reacts with  $O_2$  in aqueous electrolyte at pH 7 with a rate constant  $>10^5 M^{-1} s^{-1}$  to form  $H_2O_2$  and  $[Q]_{surf}$ . High surface area oxides functionalized with Ib yield  $[M_xO_y]-(Q)$  that can be electrochemically reduced to  $[M_xO_y]-(QH_2)$  via mediation by a low concentration of Ia in solution. The  $[M_xO_y]-(QH_2)$  can be isolated from the electrolyte solution by filtration and reacted with  $O_2/H_2O$  to yield up to 0.1 M  $H_2O_2$  in  $H_2O$  free of electrolyte. Study of the reduction of Ia at rotating-W-disk electrodes derivatized with Ib shows that the redox equilibration of the solution quinone and surface quinone is rapid. Reduction of  $[Q]_{surf}$  or Ia at visible light illuminated p- $WS_2$  can be effected at an electrode potential  $\sim 0.8$  V more positive than at a metallic electrode. The overall energetics are such that light can be used to effect the uphill formation of  $H_2O_2$  via the quinone-mediated reduction of  $O_2$ . The onset of  $O_2$  reduction is up to 0.6 V more positive than  $E^\circ(O_2/H_2O_2)$ . The sustained photoassisted reduction of  $O_2$  to  $H_2O_2$  has been demonstrated (constant output for  $>50$  h to generate  $>0.01$  M  $H_2O_2$  at  $\sim 0.5$  mA/cm $^2$  with  $\sim 100\%$  current efficiency at an electrode potential  $\sim 0.2$  V more positive than  $E^\circ(O_2/H_2O_2)$ ).

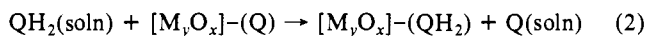
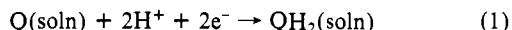
We recently communicated<sup>1</sup> results relating to the use of electrodes derivatized with Ib for the reduction of  $O_2$  to  $H_2O_2$



Ia, R = *n*-Pr  
b, R = *n*-PrSi(OMe)<sub>3</sub>

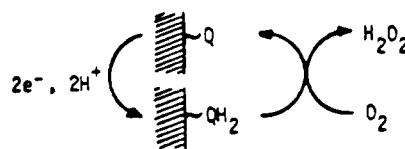
according to the mechanism represented by Scheme I. The reduction of  $O_2$  to  $H_2O_2$  with  $>90\%$  current efficiency in  $O_2$ -saturated aqueous electrolytes at pH 7.2 was found to be mass transport limited for electrode potentials such that the surface-bound quinone,  $[Q]_{surf}$ , is held in its reduced state,  $[QH_2]_{surf}$ . More than  $10^6$  molecules of  $H_2O_2$  could be made per Q unit on the surface without significant decline in cathodic current density.

We now report the complete characterization of the naphthoquinone system for reduction of  $O_2$ . Further, we show that it is possible to generate up to  $\sim 0.1$  M aqueous  $H_2O_2$  free of electrolyte and quinone via the mediated reduction of naphthoquinone units anchored to high surface area  $Al_2O_3$  or  $SiO_2$  followed by filtration and reaction of  $[SiO_2]-(QH_2)$  or  $[Al_2O_3]-(QH_2)$  with  $O_2/H_2O$ , eq 1-3. The key features of the synthetic scheme represented



by eq 1-3 are that (i)  $H_2$  is not used and the reducing power needed to make  $QH_2$  is less than that necessary to make  $H_2$ ; (ii) a low concentration of Q/ $QH_2$  in solution can be employed; and (iii) the surface-bound reductant can be separated by physical

Scheme I



means to react with aqueous  $O_2$  to give pure  $H_2O_2$  in  $H_2O$ . The procedure represented by eq 1-3 outlines a new way to synthesize  $H_2O_2$  and could be readily extended to other redox syntheses where direct (electrode) redox reaction might be undesirable.

## Experimental Section

**Materials.** Single-crystal p- $WS_2$  was generously provided by GTE Laboratories and has been characterized as having a carrier concentration of  $\sim 10^{18} cm^{-3}$ .<sup>2</sup> Single-crystal, Zn-doped ( $>10^{18} cm^{-3}$ ) p-type InP (0.5-1.0 mm thick, (111) face exposed) was provided by Dr. G. Iseler of Lincoln Laboratories and has been previously characterized.<sup>3</sup> W sheet (Alfa), 0.127 mm thick, was used for rotating-disk electrodes. Purified grade  $Na_2S_2O_4$  was obtained from Fisher Scientific Co. HPLC-grade  $CH_3CN$  (Baker) was distilled over  $P_2O_5$  before use and passed through neutral aluminum oxide (Woelm) which was dried under vacuum at 400 °C for 48 h. Electronic grade  $n-Bu_4NClO_4$  and  $Et_4NCl$  (Southwestern Analytical) were dried under vacuum at 80 °C for 24 h.  $\gamma$ -Alumina (Strem, 225 m $^2/g$ ) and silicon oxide (Alfa, 400 m $^2/g$ ) were used as received. All other chemicals were reagent grade and used as received from commercial sources.

**Synthesis of 2-Chloro-3-[[2-(dimethylamino)ethyl]amino]-1,4-naphthoquinone (II).** The synthesis of the HCl salt of II was accomplished by a previously reported procedure.<sup>4</sup> To a suspension of 22.7 g of 2,3-dichloro-1,4-naphthoquinone in 200 mL of ethanol was added 8.8 g of *N,N*-dimethylethylenediamine. The reaction mixture was stirred at room temperature overnight and then refluxed for 1 h. After cooling, a bright

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red precipitate was collected by filtration to give ~30 g (95% yield) of the crude HCl salt of II. The free base of II was then prepared by treating the crude product with excess aqueous Na<sub>2</sub>CO<sub>3</sub>, followed by extraction into CH<sub>2</sub>Cl<sub>2</sub>. The solution was dried over MgSO<sub>4</sub> and filtered. The CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum to yield II.

**Synthesis of Ia and Ib.** Ib was prepared by stirring 1 g of II in 5 mL of BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub> [prepared by reacting HC(OCH<sub>3</sub>)<sub>3</sub> with 1-bromo-3-(trichlorosilyl)propane purchased from Petrarch Chemical Co.] at 90 °C for 12 h, after which time the product precipitated from solution. Filtration and repeated washings with hexane followed by drying under vacuum yielded 1.6 g (~90%) of Ib. Ia was prepared in a manner analogous to Ib by stirring II with excess *n*-PrBr at 70 °C until the product precipitated.

The <sup>1</sup>H NMR (270 MHz; CD<sub>3</sub>OD) for Ib shows resonances at δ 0.55 (t, 2 H, silyl methylene, *J* = 8 Hz), 1.78 (m, 2 H, alkyl methylene), 3.13 (s, 6 H, *N*<sup>+</sup>-methyl), 3.33 (m, 2 H, *N*<sup>+</sup>-methylene), 3.43 (s, 9 H, silyl methoxy), 3.56 (t, 2 H, *N*<sup>+</sup>-methylene, *J* = 6.8 Hz), 4.12 (t, 2 H, *N*-methylene), 7.61 (m, 2 H, aryl), 7.90 (d, 2 H, aryl).

Elemental analysis (Galbraith) for Ib was satisfactory. Anal. Calcd for C<sub>20</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>ClSiBr: C, 46.02; H, 5.79; N, 5.37; Cl, 6.79; Si, 5.38. Found: C, 46.2; H, 5.84; N, 5.31; Cl, 6.92; Si, 5.50.

**Electrode Fabrication and Derivatization of High Surface Area Oxides and Electrodes.** Platinum wire (0.016-in. diameter), foil (0.004-in. thickness), or gauze (80 mesh) was fabricated into electrodes and pretreated<sup>5</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. W electrodes were soaked for 10 min in 1 M HNO<sub>3</sub> prior to use. p-WS<sub>2</sub> and p-InP crystals were mounted on coiled Cu wire whose leads were passed through a 4-mm glass tube.<sup>2,3</sup> All surfaces were then sealed with Epoxy-Patch 1C white epoxy (Hysol Division, Dexter Corp.) so as to leave only the surface of the semiconductor exposed. An ohmic contact to p-InP was made by ultrasonically soldering (Sonobond Corp.) with a 1:1 In:Cu alloy followed by attachment of a Cu wire with In solder.<sup>3</sup> Ohmic contact to p-WS<sub>2</sub> was made by using Ag epoxy.<sup>2</sup> The InP electrodes were etched in ~1 mM Br<sub>2</sub> in CH<sub>3</sub>OH for 60 s at 25 °C prior to use. The p-WS<sub>2</sub> electrodes were not etched prior to use, since fresh surfaces are exposed in the fabrication procedure.

Platinization of p-InP was accomplished by passing ~2 × 10<sup>-2</sup> C/cm<sup>2</sup> of cathodic charge at an illuminated (~40 mW/cm<sup>2</sup>; 632.8 nm) p-InP electrode potentiostatted at 0.0 V vs. SCE in an O<sub>2</sub>-free, aqueous 0.1 M NaClO<sub>4</sub> solution containing ~1.5 mM K<sub>2</sub>PtCl<sub>6</sub>.

Electrodes and powders were derivatized for 10–24 h in dry CH<sub>3</sub>CN with 1–5 mM Ib. For concentrations of Ib near 5 mM addition of H<sub>2</sub>O (~1% by weight) was necessary to dissolve the reagent. The materials to be derivatized were suspended in the solution of Ib without stirring at 25 °C. After derivatization the electrodes and powders were washed with H<sub>2</sub>O until no further quinone was removed.

**Equipment and Procedures.** Electrochemical and illumination equipment has been described previously.<sup>2,3</sup> For cyclic voltammograms a single-compartment cell was used with a standard three-electrode configuration with either Pt, W, p-WS<sub>2</sub>, or p-InP as a cathode, a Pt anode, and either an Ag/Ag<sup>+</sup> reference electrode (a silver wire immersed in 0.01 M AgNO<sub>3</sub>/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at +0.35 V vs. SCE) or an SCE. Controlled potential electrolyses were carried out in a two-compartment cell in which the Pt cathode was isolated by an ultrafine glass frit.

NMR spectra were recorded on a Bruker 270-MHz Fourier transform spectrometer. The UV-vis photoacoustic spectra were recorded on a PAR Model 6001 spectrometer following previously described procedures.<sup>6</sup> Derivatized SiO<sub>2</sub> samples were diluted with MgO prior to recording the spectra to make the sample sufficiently dilute that the photoacoustic signal is approximately proportional to the percent light absorbed. Nonidealities in the optical system were corrected by dividing the spectra by a reference spectrum of carbon black. UV-vis solution spectra were recorded on a Cary 17 spectrophotometer using 1.0-cm path quartz optical cells. IR photoacoustic spectra of SiO<sub>2</sub> derivatized with Ib were recorded on a Nicolet 7199 Fourier transform spectrometer. A reasonably good match was obtained in the CO stretch region (1500–2000 cm<sup>-1</sup>) to KBr pellet spectra of Ia recorded on a Perkin-Elmer Model 180 spectrometer.

**Determination of H<sub>2</sub>O<sub>2</sub>.** Small volumes of solutions containing H<sub>2</sub>O<sub>2</sub> were diluted with H<sub>2</sub>O containing an excess of Ti(VI) ions. The optical density at 405 nm corresponding to the Ti(IV)–H<sub>2</sub>O<sub>2</sub> complex was used to determine H<sub>2</sub>O<sub>2</sub> concentrations. Control analyses using authentic samples of H<sub>2</sub>O<sub>2</sub> were run to ensure the reliability of the technique.

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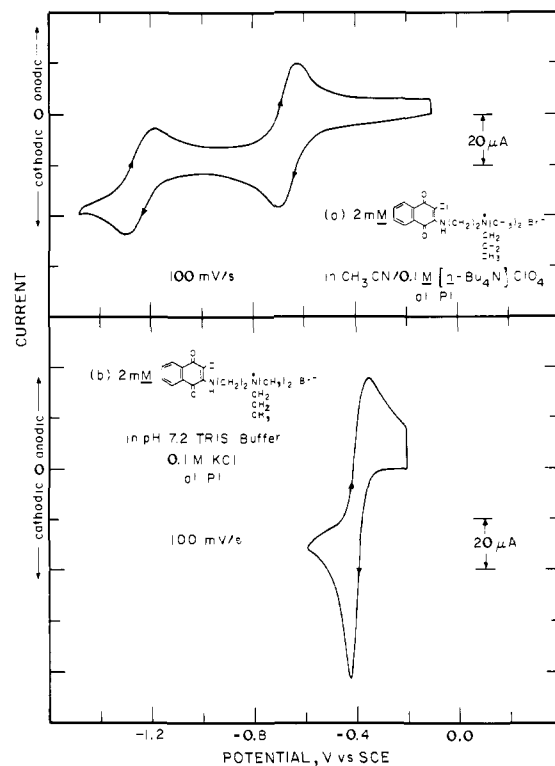


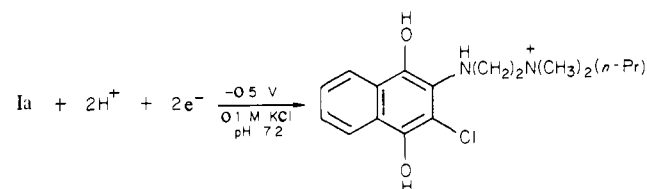
Figure 1. Cyclic voltammetry of Ia.

Standard solutions of H<sub>2</sub>O<sub>2</sub> for preparation of calibration curves for the Ti(IV) analyses were prepared by using reagent grade H<sub>2</sub>O<sub>2</sub>, and their H<sub>2</sub>O<sub>2</sub> concentration was determined by titration with standard solutions of KMnO<sub>4</sub>.

## Results

**Solution Electrochemistry of Ia and the Use of Ia as a Solution Mediator for Reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>.** We have found the electrochemistry of Ia to be very well-defined in both aqueous and nonaqueous media. Figure 1 shows the cyclic voltammetry for this reagent at a Pt electrode. In dry CH<sub>3</sub>CN/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> two reversible, one-electron reductions characteristic of quinones, Figure 1a, are found. The *E*<sup>o</sup>'s in CH<sub>3</sub>CN/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> are at -1.25 and -0.65 V vs. SCE. We approximate the *E*<sup>o</sup> value to be the average position of the anodic and cathodic current peaks. In aqueous 0.1 M KCl/pH 7.2 and at the same Pt electrode, the same concentration of Ia gives a single wave more positive in potential and roughly twice the area of each of the waves in CH<sub>3</sub>CN/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>, Figure 1b, confirming the 2e<sup>-</sup> process expected for quinones in aqueous media. Reduction of 1 mM Ia in CH<sub>3</sub>CN/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> at a rotating Pt disk ( $\omega^{1/2} = 10$  (rad/s)<sup>1/2</sup>) results in two current plateaus of equivalent height, consistent with the two, well-separated one-electron cyclic voltammetry waves. In aqueous 0.1 M KCl/pH 7.2, reduction of 1 mM Ia at the same rotating disk ( $\omega^{1/2} = 10$  (rad/s)<sup>1/2</sup>) results in only one limiting current plateau that coincides in height with the overall two-electron limiting current in CH<sub>3</sub>CN/0.1 M *n*-Bu<sub>4</sub>NClO<sub>4</sub>. Further, the potential of the reduction wave for Ia in aqueous KCl is found to vary by ~60 mV per pH unit over the range pH 4–9 as is expected for the 2e–2H<sup>+</sup> reduction. The *E*<sup>o</sup> at pH = 7.2 is -0.38 V vs. SCE.

The current efficiency for the reduction of Ia to the dihydroxy species, eq 4, was determined at a Pt cathode held at -0.5 V vs.

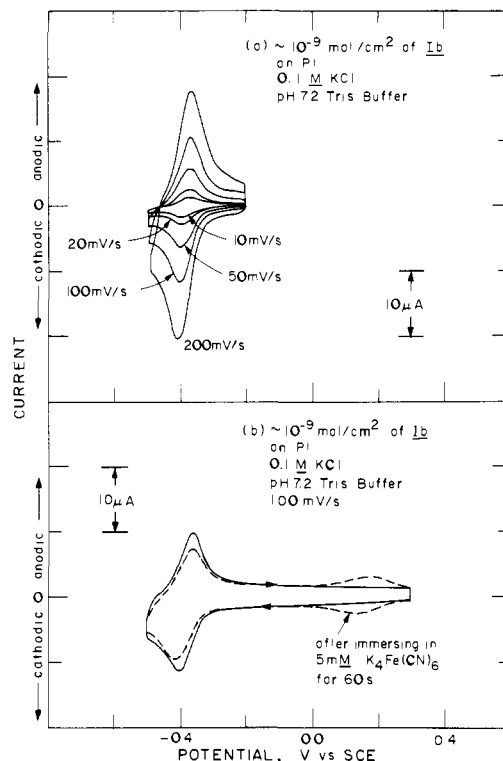


SCE in a two-compartment cell containing 0.1 M KCl/pH 7.2 with 0.15 mM Ia in the catholyte. By monitoring the decrease in optical density of the catholyte at 460 nm (corresponding to Ia) as a function of charge passed we have determined that the  $2e^-2H^+$  reduction process occurs with 100% current efficiency, within experimental error. Exposure of the solution to  $O_2$  rapidly and quantitatively regenerates Ia and yields a stoichiometric amount of  $H_2O_2$ .

An examination of an  $O_2$ -saturated 0.1 M KCl/pH 7.2 aqueous solution of 1.0 mM Ia at a rotating-W-disk electrode reveals that the rate of the solution reaction of the reduced form of Ia with  $O_2$  is very fast. The study of Ia in the presence of  $O_2$  was carried out at a W electrode, since there is negligible current attributable to  $O_2$  reduction without Ia. In the presence of Ia a plot of the plateau current vs.  $\omega^{1/2}$  is a straight line with zero intercept for an electrode potential more negative than  $\sim -0.6$  V vs. SCE. The absolute current density is consistent with a mass transport limited reduction of the  $O_2$ /Ia material available up to a rotation speed of 1900 rpm. Further, a cyclic voltammogram at W in the same solution shows a cathodic current peak  $\sim 60$  mV more positive than the peak for reduction of Ia at a sweep rate of 20 mV/s.<sup>8a</sup> The catalytic prewave is consistent with a very fast homogeneous reduction of the  $O_2$  via the dihydroxy product from reducing Ia. Thus, the reduction of Ia in the presence of  $O_2$  comprises a classic solution EC' system<sup>8b</sup> where Ia is reduced and regenerated in an irreversible following reaction with  $O_2$  leading to  $H_2O_2$  formation.

**Behavior of Electrodes Derivatized with Ib and Mediated Reduction of  $O_2$  to  $H_2O_2$  at Derivatized Electrodes.** As reported previously,<sup>1</sup> the behavior of electrodes bearing approximately monolayer amounts ( $\sim 10^{-10}$  mol/cm<sup>2</sup>) of Ib is well-defined in aqueous media. The  $[Q/QH_2]_{surf}$  system has an  $E^{\circ'}$  within 50 mV of the  $E^{\circ'}$  for Ia as measured by cyclic voltammetry at Pt, and exhibits the expected  $\sim 60$  mV/pH unit shift. The peak current is directly proportional to sweep rate below 50 mV/s, and the electrodes are durable for thousands of cycles between the oxidized and reduced forms. In nonaqueous media ( $CH_3CN$ ,  $N,N$ -dimethylformamide or dimethyl sulfoxide with 0.1 M  $n-Bu_4NClO_4$  or  $[Et_4N]Cl$ ), however, the two one-electron waves for  $[Q/Q^{\cdot-}/Q^{2-}]_{surf}$  are quite broad and ill-defined. One possible explanation is that the structure of  $[Q]_{surf}$  is changed sufficiently on going from aqueous to nonaqueous media that charge transport and/or ion flow becomes slow. Solvent effects on the electrochemistry of surface-modified electrodes have been previously documented.<sup>9</sup>

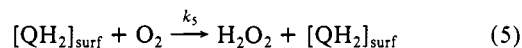
Figure 2 shows the cyclic voltammetry for a derivatized electrode bearing significantly greater than monolayer coverage of the  $[Q/QH_2]_{surf}$ . The larger coverages can be achieved by longer derivatization times. Electrodes bearing polymeric quantities of the  $[Q/QH_2]_{surf}$  system from reaction with Ib can firmly bind large transition-metal complexes such as  $Fe(CN)_6^{3-/4-}$ , as illustrated in Figure 2. The firm binding of such complex anions can be attributed to the positive charge on the Q units. Such electrostatic binding of large anions to electrode-confined, positively charged polymers is now commonplace.<sup>10</sup> The interesting point here is that it appears that the electrostatically bound  $Fe(CN)_6^{3-/4-}$  system is present in an amount consistent with near perfect charge compensation of the polymer via the  $Fe(CN)_6^{3-/4-}$ . This conclusion is based on the relative charge passed in the  $[Q]_{surf} \rightleftharpoons [QH_2]_{surf}$  interconversion compared to that for the  $Fe(CN)_6^{3-} \rightleftharpoons Fe(CN)_6^{4-}$  interconversion. This is consistent with the conclusion that the integration of the cyclic voltammogram for the  $[Q]_{surf} \rightleftharpoons [QH_2]_{surf}$  interconversion gives the amount of material on the surface and



**Figure 2.** Cyclic voltammetry of an electrode derivatized with Ib showing the  $-0.40$  V vs. SCE wave associated with the  $[Q/QH_2]_{surf}$  couple and the response for the bound  $Fe(CN)_6^{3-/4-}$  couple at  $\sim +0.2$  V vs. SCE.

that it is all electrochemically active.

We have shown by rotating-disk experiments with derivatized W electrodes that  $O_2$  can be reduced with a minimum heterogeneous rate constant of 0.013 cm/s at an electrode potential of  $-0.5$  V vs. SCE.<sup>1</sup> The reduction of  $O_2$  to  $H_2O_2$  is mass transport limited up to a rotation speed of 1900 rpm at a derivatized W disk bearing about  $\sim 10^{-10}$  mol/cm<sup>2</sup> of the  $[Q/QH_2]_{surf}$  held in the  $[QH_2]_{surf}$  state for a pH range of 5.8–8. The minimum heterogeneous rate constant is deduced from the strict linearity of the plot of limiting current against (rotation velocity)<sup>1/2</sup>.<sup>11</sup> Note that the rate constant does not have the usual potential dependence, because we hypothesize that it is the molecular entities it that react with  $O_2$ . The lower limit then on the rate constant,  $k_s$ , for eq 5



is  $0.65 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>. The reduction of  $O_2$  at derivatized W is also mass transport limited in  $D_2O$  solvent. A detailed study of the rate of reaction of  $O_2$  with  $[QH_2]_{surf}$  is under way and will be reported elsewhere. The rate of  $O_2$  reduction slows when the coverage of  $[Q/QH_2]_{surf}$  is  $> \sim 10^{-9}$  mol/cm<sup>2</sup>, presumably owing to relatively slow charge transport through the polymer. This is consistent with cyclic voltammetry at high sweep rates that shows sluggish kinetics for the  $[Q]_{surf} \rightleftharpoons [QH_2]_{surf}$  interconversion at high coverages.

The two-stimuli response of a p-type semiconductor<sup>12</sup> electrode can be used to prove that the  $[QH_2]_{surf}$  is oxidized by reaction with  $O_2$ . Figure 3 shows the data for a derivatized p-WS<sub>2</sub> electrode. The p-WS<sub>2</sub> electrode is blocking to reduction in the dark, but upon illumination with light of energy greater than the band gap ( $E_g \approx 1.3$  eV) the reduction of  $[Q]_{surf}$  can be effected at an electrode potential  $\sim 0.8$  V less reducing than at a metallic electrode such as Pt or W. At the negative limit of the scan, the light is blocked and the dark  $[QH_2]_{surf} \rightarrow [Q]_{surf}$  process occurs on the return sweep. In the presence of  $O_2$  (dashed curve) the

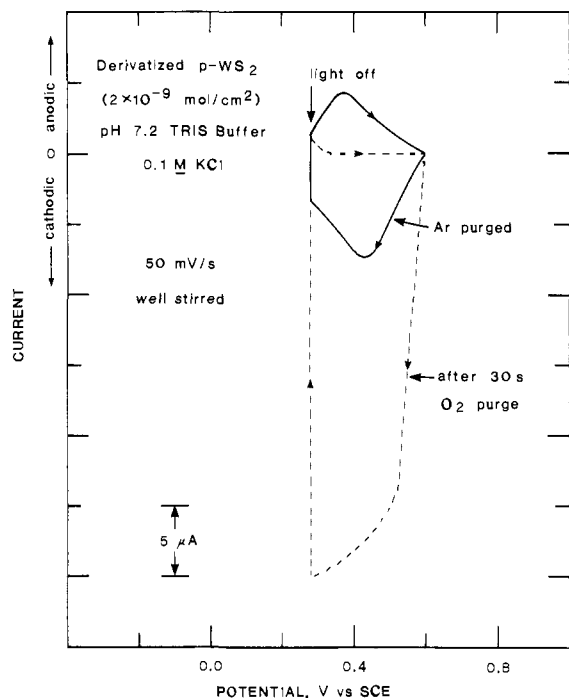
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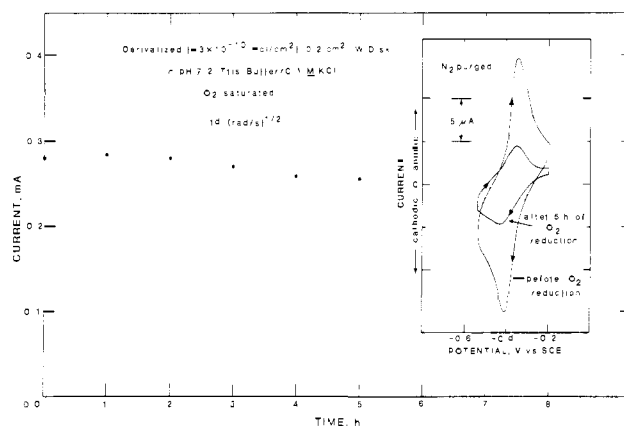
**Figure 3.** Cyclic voltammery for illuminated (632.8 nm;  $\sim 40$  mW/cm<sup>2</sup>) derivatized p-WS<sub>2</sub> without O<sub>2</sub> (—) and with O<sub>2</sub> (- -). At the cathodic limit of each scan the light has been switched off. The absence of the [QH<sub>2</sub>]<sub>surf</sub> → [Q]<sub>surf</sub> anodic peak in the presence of O<sub>2</sub> evidences the reaction of O<sub>2</sub> with the photogenerated [QH<sub>2</sub>]<sub>surf</sub>.

derivatized p-WS<sub>2</sub> gives more photocurrent than that associated with [Q]<sub>surf</sub> → [QH<sub>2</sub>]<sub>surf</sub>, consistent with the mediated reduction of O<sub>2</sub>. The key point, however, is that in the presence of O<sub>2</sub> there is no return wave for [QH<sub>2</sub>]<sub>surf</sub> → [Q]<sub>surf</sub>, indicating that [QH<sub>2</sub>]<sub>surf</sub> is indeed being oxidized by O<sub>2</sub> and at a rate which is competitive with oxidation by the electrode.

Disk electrodes have also been used to examine the reduction of Ia, as noted above. Naked W disks show mass transport limited reduction of 5 mM Ia in 0.1 M KCl/pH 7.2 at electrode potentials negative of -0.5 V vs. SCE for rotation speeds up to 1900 rpm. Likewise, W disks derivatized with Ib ( $\leq 1 \times 10^{-9}$  mol/cm<sup>2</sup>) show mass transport limited reduction of Ia for electrode potentials negative of -0.5 V vs. SCE. These data show that the heterogeneous rate constant for reduction of Ia is at least  $\sim 0.013$  cm/s.<sup>11</sup> In the derivatized disk case, the data are consistent with the conclusion that the rate constant for reduction of Ia by [QH<sub>2</sub>]<sub>surf</sub> is at least  $0.65 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>.

The mediated reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> at derivatized W electrodes can be sustained for prolonged periods of time. Figure 4 shows data from such an experiment for a W rotating disk electrode at  $\omega^{1/2} = 14.0$  (rad/s)<sup>1/2</sup> held at -0.5 V vs. SCE in 10 mL of O<sub>2</sub>-saturated 0.1 M KCl/pH 7.2 catholyte in a two-compartment cell. There is a slight decline in current over the 5-h period shown, but the total charge passed represents  $> 10^6$  turnovers of [Q/QH<sub>2</sub>]<sub>surf</sub>. This resulted in the formation of  $\sim 2$  mM H<sub>2</sub>O<sub>2</sub> with  $> 90\%$  current efficiency. The inset shows the cyclic voltammery for the derivatized electrode in the absence of O<sub>2</sub> both before and after the mediation. From the difference in size of the two waves, we conclude that the mediated reduction of O<sub>2</sub> resulted in loss of  $\sim 50\%$  of [Q]<sub>surf</sub>. The small decline in current density observed even with this large loss of [Q]<sub>surf</sub> is not surprising, however, since the reduction of O<sub>2</sub> is mass transport limited under the conditions employed. Consequently, the observed reduction current will not be a simple function of electrode coverage.

**Electrochemical Reduction of Naphthoquinone Anchored to High Surface Area Oxides.** The direct reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> using electrodes derivatized with Ib is efficient and can be sustained to generate significant concentrations of H<sub>2</sub>O<sub>2</sub>. Even at 0.1 M H<sub>2</sub>O<sub>2</sub>, the W/[Q/QH<sub>2</sub>]<sub>surf</sub> electrodes will effect O<sub>2</sub> reduction competitively with reduction of the H<sub>2</sub>O<sub>2</sub>.<sup>1</sup> However, the elec-



**Figure 4.** Steady-state reduction of O<sub>2</sub> at a derivatized, rotating-W-disk electrode. Inset shows the cyclic voltammery corresponding to the [Q]<sub>surf</sub> ⇌ [QH<sub>2</sub>]<sub>surf</sub> interconversion before and after the steady-state reduction for 5 h.

trochemical reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> by necessity means the H<sub>2</sub>O<sub>2</sub> solution will contain supporting electrolyte, and high concentrations of H<sub>2</sub>O<sub>2</sub> do give more rapid decline in catalytic activity of the [Q/QH<sub>2</sub>]<sub>surf</sub> system. In order to circumvent the problem of having the electrolyte as an impurity we have adopted the strategy represented by eq 1-3 in the introduction. Additionally, this strategy avoids prolonged contact of the [Q/QH<sub>2</sub>]<sub>surf</sub> system with high concentrations of H<sub>2</sub>O<sub>2</sub>. Basically, the objective is to heterogenize the QH<sub>2</sub> on high surface area material to facilitate its separation from the electrolyte solution. The solid bearing the QH<sub>2</sub> functionality can be exposed to O<sub>2</sub>/H<sub>2</sub>O to prepare H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O that is free of electrolyte. The resulting suspension of surface-confined Q can then be separated by filtration from the H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O solution. High surface area Al<sub>2</sub>O<sub>3</sub> (225 m<sup>2</sup>/g) and SiO<sub>2</sub> (400 m<sup>2</sup>/g) have been employed as materials to which the Q/QH<sub>2</sub> system can be covalently anchored. Both Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are inert to H<sub>2</sub>O<sub>2</sub> and do not decompose H<sub>2</sub>O<sub>2</sub>. The high surface area means that a significant fraction of the mass of the derivatized surface can in fact be the Q/QH<sub>2</sub> system.

High surface area SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> can be derivatized by using Ib to yield [SiO<sub>2</sub>]-Q or [Al<sub>2</sub>O<sub>3</sub>]-Q, respectively.<sup>13</sup> The colorless powders become orange upon derivatization with Ib. Figure 5 shows a comparison of the optical properties of Ia in H<sub>2</sub>O and [SiO<sub>2</sub>]-Q as a powder. Obviously, the spectral features are similar and consistent with the conclusion that the quinone is intact upon attachment to the surface, as expected, based on the electrochemical data for electrodes derivatized with Ib. The infrared spectra of the [SiO<sub>2</sub>]-Q and [Al<sub>2</sub>O<sub>3</sub>]-Q powders also accord well with the infrared spectra for Ia. Finally, the [Al<sub>2</sub>O<sub>3</sub>]-Q was analyzed and found to be  $\sim 0.1$  mmol of Q/g of material. This is about an order of magnitude below the Q content in pure Ib, which is  $\sim 2$  mmol/g of material.

The [Al<sub>2</sub>O<sub>3</sub>]-Q and [SiO<sub>2</sub>]-Q are durable and can be washed repeatedly with aqueous electrolyte or with H<sub>2</sub>O without removal of Q. Importantly, the [SiO<sub>2</sub>]-Q and [Al<sub>2</sub>O<sub>3</sub>]-Q are durable to reduction and subsequent oxidation with O<sub>2</sub>. For example, aqueous S<sub>2</sub>O<sub>4</sub><sup>2-</sup> can be used to reduce the surface-bound quinone by adding Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to a suspension of the [M<sub>y</sub>O<sub>x</sub>]-Q in deoxygenated H<sub>2</sub>O. The orange powder becomes off-white almost instantly upon mixing, consistent with the chemistry represented by eq 6. Filtering the solution to isolate the off-white [M<sub>y</sub>O<sub>x</sub>]-Q + S<sub>2</sub>O<sub>4</sub><sup>2-</sup> + 2H<sup>+</sup> → [M<sub>y</sub>O<sub>x</sub>]-Q(H<sub>2</sub>) + 2SO<sub>2</sub> (6)

powder under N<sub>2</sub> followed by washing the powder with deoxygenated H<sub>2</sub>O yields an off-white powder. The off-white color is consistent with [M<sub>y</sub>O<sub>x</sub>]-Q(H<sub>2</sub>), since reduction of Ia in aqueous electrolyte solutions gives the dihydroxy compound, eq 4, that has no visible absorption maximum. Exposure of the off-white powder from S<sub>2</sub>O<sub>4</sub><sup>2-</sup> reduction to a known volume of O<sub>2</sub>-saturated H<sub>2</sub>O

Table I. Chemical and Mediated Electrochemical Reduction of  $[M_xO_y]-(Q)$  to  $[M_xO_y]-(QH_2)$  To Reduce  $O_2$  to  $H_2O_2$ 

powder (mass, g) <sup>a</sup>	solution volume, mL <sup>b</sup>	reduction method <sup>c</sup>	charge passed, C <sup>d</sup>	$H_2O_2$ detected, M <sup>e</sup>	efficiency <sup>f</sup>
$[Al_2O_3]-(Q)$ (1.0) <sup>g</sup>	5.0 <sup>g</sup>	mediation, 5 mM Ia <sup>g</sup>	23.0 <sup>g</sup>	0.02 <sup>g</sup>	90 <sup>g</sup>
$[Al_2O_3]-(Q)$ (1.0)	8.0	mediation, 0.5 mM Ia	14.3	0.01	100
$[Al_2O_3]-(Q)$ (0.5)	8.0	mediation, 0.5 mM Ia	7.5	0.005	100
$[Al_2O_3]-(Q)$ (1.0)	0.5	$S_2O_4^{2-}$		0.095	>90
$[SiO_2]-(Q)$ (1.0)	5.0	$S_2O_4^{2-}$		0.012	>80
$[SiO_2]-(Q)$ (0.5)	2.0	$S_2O_4^{2-}$		0.015	>90

<sup>a</sup> High surface area  $SiO_2$  or  $Al_2O_3$  derivatized with Ib. Analysis shows  $\sim 0.1$  mmol of Q/g of derivatized powder. <sup>b</sup> Volume of oxygenated  $H_2O$  added to  $[M_xO_y]-(QH_2)$ . In the case of the electrochemical reduction this is also the volume of the catholyte solution used in the experiment. <sup>c</sup> "Mediation" refers to the electrochemical reduction of a suspension of  $[M_xO_y]-(Q)$  in 0.1 M KCl/pH 7.2 containing the indicated concentration of Ia. The reduction is carried out at a Pt electrode at  $-0.5$  V vs. SCE in a two-compartment cell with the  $[M_xO_y]-(Q)$  and Ia in the cathode compartment. Reduction with  $S_2O_4^{2-}$  was carried out by adding excess  $Na_2S_2O_4$  to an aqueous suspension of  $[M_xO_y]-(Q)$  followed by filtering and washing with deoxygenated  $H_2O$ . Finally, the indicated volume of  $H_2O$  was used to suspend the  $[M_xO_y]-(QH_2)$  and  $O_2$  was added. <sup>d</sup> Charge passed in the mediated electrochemical reduction. Includes  $QH_2$  and  $[M_xO_y]-(QH_2)$  formation. <sup>e</sup>  $H_2O_2$  concentration detected in the volume indicated. For mediated electrochemical reduction the  $H_2O_2$  comes from both  $QH_2$  and  $[M_xO_y]-(QH_2)$  reaction with  $O_2$ . For the  $S_2O_4^{2-}$  reduction  $[M_xO_y]-(QH_2)$  was isolated in a pure state prior to reaction with  $O_2/H_2O$ . <sup>f</sup> Based on the total  $QH_2$  available for reaction with  $O_2$ . <sup>g</sup> These data correspond to the plot in Figure 6.

regenerates the orange color, and analysis of the aqueous solution shows a concentration of  $H_2O_2$  consistent with the amount of Q initially present as  $[M_xO_y]-(Q)$ . The highest concentration of  $H_2O_2$  achieved by this procedure has been  $\sim 0.1$  M  $H_2O_2$  in electrolyte-free  $H_2O$ . Note that the material from derivatization with Ib always has a compensating anion, since the reagent has a positive charge. However, when aqueous  $O_2$  reacts with  $[M_xO_y]-(QH_2)$  there is no additional electrolyte necessary. Interestingly, vacuum-dried ( $25^\circ C$ )  $[Al_2O_3]-(QH_2)$ , produced via  $S_2O_4^{2-}$  reduction of  $[Al_2O_3]-(Q)$ , does not react at  $25^\circ C$  with gas-phase  $O_2$  or with  $O_2$  in dry  $CH_3CN$ . Lack of reaction is evidenced in this case by the failure to regenerate the orange color characteristic of  $[Al_2O_3]-(Q)$ . The same  $[Al_2O_3]-(QH_2)$  that fails to react with gas-phase  $O_2$  or  $O_2$  in  $CH_3CN$  reacts promptly with aqueous  $O_2$ . Addition of a small amount of  $O_2$ -saturated  $H_2O$  to a suspension of  $[M_xO_y]-(QH_2)$  in dry  $CH_3CN$  results in rapid formation of  $[M_xO_y]-(Q)$ .

The  $[M_xO_y]-(Q)$  powders are not electroactive as a suspension in aqueous (pH 7.2) electrolyte solution. The addition, for example, of 1.0 g of  $[Al_2O_3]-(Q)$  to 10 mL of a 0.1 M KCl/pH 7.2 electrolyte solution gives no increase in current for a Pt gauze electrode held at  $-0.5$  V vs. SCE. This underscores the fact that the Q/ $QH_2$  system is persistently attached to the  $M_xO_y$  surface, since quinone in solution is electroactive. The reduction of the surface-bound quinone, however, can be effected by using Ia as a solution mediator. Data in Figure 6 show that the mediated reduction of the surface-bound quinone can be effected in the cathode compartment of a two-compartment cell by having 5 mM Ia in the electrolyte solution. The charge passed associated with reducing Ia +  $[Al_2O_3]-(Q)$  is consistent with the total amount of quinone present. The ability of Ia to serve as a mediator is consistent with its own electrochemical behavior at Pt and with the ability to reduce Ia at a mass transport limited rate at a rotating-disk electrode derivatized with Ib. Addition of  $O_2$  to the solution after generation of the dihydroxy product from Ia and the  $[Al_2O_3]-(QH_2)$  results in the formation of  $H_2O_2$  in an amount consistent with the total available  $QH_2$ . Table I summarizes the results of several such experiments, including experiments using  $S_2O_4^{2-}$  to reduce the  $[M_xO_y]-(Q)$  to  $[M_xO_y]-(QH_2)$ . As indicated in the mediation experiments, significantly more  $H_2O_2$  is made than Ia initially present. The derivatized powders are durable, and even in the presence of 0.1 M  $H_2O_2/H_2O$  do not undergo decomposition on the several-minute time scale required to remove the  $[M_xO_y]-(Q)$  by filtration.

**Photoassisted Reduction of Ia and  $[Q]_{surf}$ .** As previously reported<sup>1</sup> and shown in Figure 3, p- $WS_2$  can be derivatized with Ib. Irradiation (632.8 nm;  $\sim 40$  mW/cm<sup>2</sup>) of the derivatized p- $WS_2$  results in a reduction wave at  $\sim +0.4$  V vs. SCE in deoxygenated 0.1 M KCl/pH 7.2 solution attributable to the  $[Q]_{surf} \rightarrow [QH_2]_{surf}$  reduction. The difference in reduction current peak positions on a reversible electrode,  $-0.4$  V vs. SCE, and the peak for illuminated p- $WS_2$  is  $\sim 0.8$  V, the extent to which light can be used to drive the reduction of  $[Q]_{surf}$  to  $[QH_2]_{surf}$  in an uphill

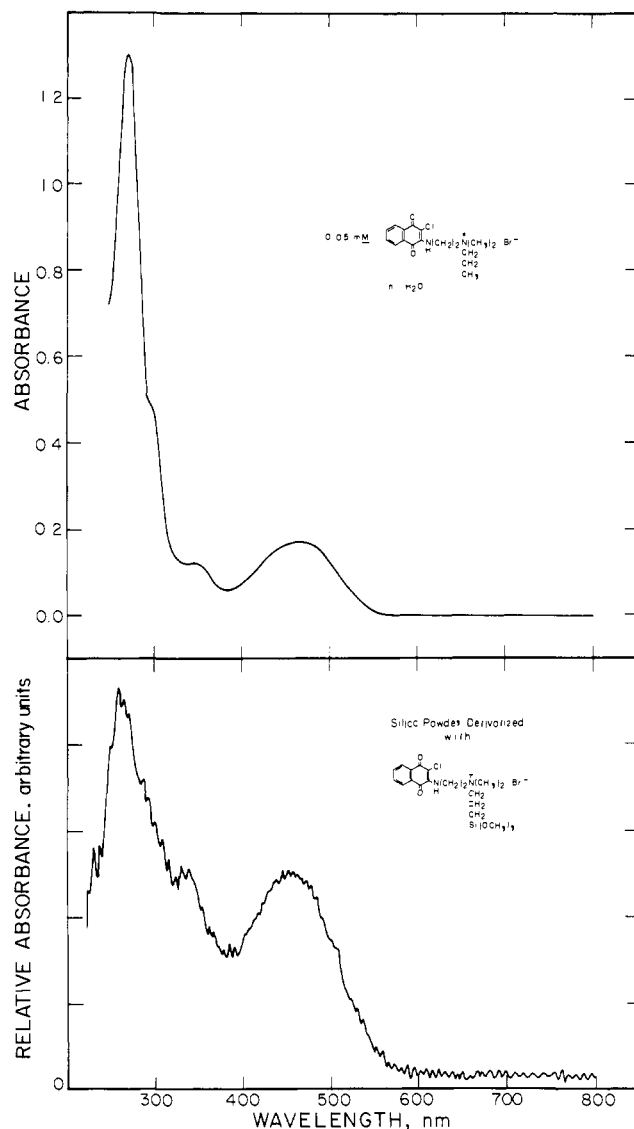
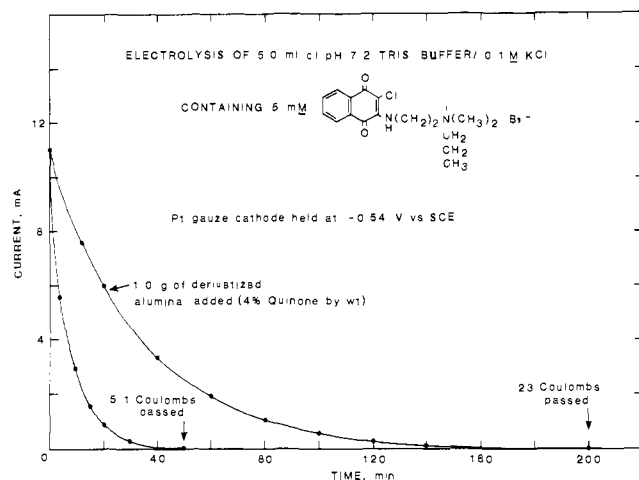


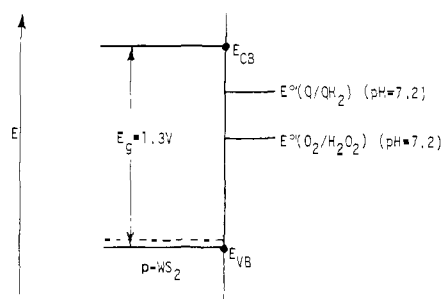
Figure 5. Optical absorption (1.00-cm path) of Ia in  $H_2O$  (top) and photoacoustic spectrum of  $[SiO_2]-(Q)$  (bottom).

sense. The  $\sim 0.8$ -V photovoltage on p- $WS_2$  is about what is expected on the basis of the photovoltage reported for other redox couples in the same potential regime.<sup>2</sup> The band gap of p- $WS_2$  is  $\sim 1.3$  eV, and thus a photovoltage of  $\sim 0.8$  V suggests a relatively efficient energy transduction process. The p- $WS_2$  surface is relatively free of oxide and the mode of attachment is not clear. Treatment of the p- $WS_2$  with Ia in the same manner as Ib results



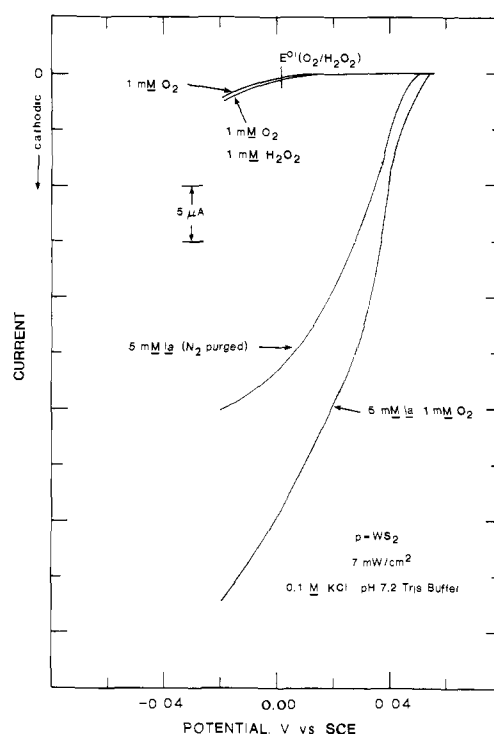
**Figure 6.** Plot of cathodic current vs. time for a Pt electrode in the cathode compartment of a two-compartment cell. The catholyte contained 5 mM Ia corresponding to 5.1 C or 5 mM Ia and 1.0 g of [Al<sub>2</sub>O<sub>3</sub>]-Q (~0.1 mmol of Q) corresponding to 23 C. Cf. text and first entry in Table I.

## Scheme II



in no electrochemically detectable surface-confined material. This indicates that the  $-\text{Si}(\text{OCH}_3)_3$  group of Ib is essential to the attachment of the quinone. It is likely that oligomerization of Ib occurs and the "attached" material is in fact precipitated onto the electrode surface. The  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  system is fragile as evidenced by rapid loss of electrochemical response for the  $[\text{Q}]_{\text{surf}} \rightleftharpoons [\text{QH}_2]_{\text{surf}}$  interconversion. Loss of ~50% of the electrochemically detected  $[\text{Q}]_{\text{surf}}$  after 25  $[\text{Q}]_{\text{surf}} \rightleftharpoons [\text{QH}_2]_{\text{surf}}$  interconversions is not atypical, but occasionally a photoelectrode will show persistent electroactivity for the  $[\text{Q}/\text{QH}_2]_{\text{surf}}$  system.

The  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  electrodes will effect the reduction of O<sub>2</sub> in aqueous 0.1 M KCl/pH 7.2 under conditions where the nonderivatized electrode gives negligible response to O<sub>2</sub>. Thus, the  $[\text{Q}/\text{QH}_2]_{\text{surf}}$  is a catalyst for the photoelectrode in a manner similar to that for the metallic electrodes. A difference is that illumination of the derivatized  $\text{p-WS}_2$  allows the uphill reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. The electrode potential at which the  $[\text{Q}]_{\text{surf}}$  can be reduced to  $[\text{QH}_2]_{\text{surf}}$  is ~0.4 V positive of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2) = \sim +0.02$  V vs. SCE at pH 7.2. Scheme II shows a representation of the key aspects of the interface energetics. The point is that the effective position of the conduction band edge,  $E_{\text{CB}}$ , is such that both  $[\text{Q}]_{\text{surf}}$  and O<sub>2</sub> can be reduced with electrons excited by  $\geq E_g$  energy light. The energy conversion efficiency with respect to the O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> couple is controlled by the relative positions of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$  and the valence band edge,  $E_{\text{VB}}$ . Thus, the  $E^{\circ}$  for a redox mediator system for the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> could be situated anywhere between  $E_{\text{CB}}$  and  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$  and still yield the best performance from the photoelectrode. By way of contrast, the optimum performance for a metallic electrode occurs when the mediation system allows reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> at an electrode potential just negative of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$ . As can be seen in Figure 3, the onset of O<sub>2</sub> reduction at illuminated  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  electrodes occurs at  $\sim +0.6$  V vs. SCE. Thus, the O<sub>2</sub> reduction can be effected ~600 mV more positive than the  $E^{\circ}$  for (O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>). Unfortunately, the durability of derivatized



**Figure 7.** Photocurrent-voltage curves for naked  $\text{p-WS}_2$  in the presence of O<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, Ia, and Ia/O<sub>2</sub>.

$\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  electrodes is not sufficiently great to allow the sustained generation of significant quantities of H<sub>2</sub>O<sub>2</sub>. However, the initial photocurrent-voltage curves do show that the light can be used to contribute to the energy needed to reduce O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> using a  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  photocathode. For any potential positive of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$  where there is photocurrent,  $i$ , corresponding to O<sub>2</sub> → H<sub>2</sub>O<sub>2</sub>, light energy reduces the thermodynamically required electrical energy needed to reduce O<sub>2</sub>. The extent to which photocurrent is observed positive of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$  is the photovoltage,  $E_V$ . The maximum optical power conversion efficiency,  $\eta_{\text{max}}$ , is given by eq 7 where  $(E_V \times i)_{\text{max}}$  is

$$\eta_{\text{max}} = \frac{(E_V \times i)_{\text{max}}}{\text{optical power in}} \quad (7)$$

the maximum value of photocurrent times photovoltage.  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  photocathodes for the photoassisted reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> give  $\eta_{\text{max}} = 2-3\%$  for an input optical power density of  $\sim 10$  mW/cm<sup>2</sup> at 632.8 nm for a stirred, O<sub>2</sub>-saturated, 0.1 M KCl/pH 7.2 solution. The value of  $\eta_{\text{max}}$  declines with increasing light intensity due to the limited concentration of O<sub>2</sub> in the solution.

While the  $\text{p-WS}_2/[\text{Q}/\text{QH}_2]_{\text{surf}}$  photocathodes are not durable for the photoassisted reduction of O<sub>2</sub>, we do find that naked  $\text{p-WS}_2$  photocathodes can be used to effect the sustained generation of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> when Ia is present in solution, Figure 7. The reduction of O<sub>2</sub> can be effected with constant output parameters for periods of >50 h at  $\sim 0.5$  mA/cm<sup>2</sup> to generate >0.01 M H<sub>2</sub>O<sub>2</sub> at  $\sim 100\%$  current efficiency at an  $\eta_{\text{max}} \approx 2\%$  (632.8 nm;  $\sim 10$  mW/cm<sup>2</sup>). In such experiments the electrode potential can be held at least 200 mV positive of  $E^{\circ}(\text{O}_2/\text{H}_2\text{O}_2)$ . Again, the value of  $\eta_{\text{max}}$  declines with increasing light intensity, owing to the low solubility of O<sub>2</sub>. The point is that at high light intensity the photocurrent is limited by mass transport of the Ia/O<sub>2</sub>, not by the light intensity. Consequently, the quantum yield for electron flow declines at high light intensity. The photoassisted mediated reduction of O<sub>2</sub> via Ia in solution is consistent with the behavior of Ia/O<sub>2</sub> in solution at metallic electrodes (vide supra).

The ability to effect the uphill reduction of Ia at  $\text{p-WS}_2$  is established by data included in Figure 7. This shows that light can be used to contribute to the energy needed to effect the reduction of suspensions of  $[\text{M}_x\text{O}_y]-(\text{Q})$  as has been done with the metallic electrodes. In the absence of O<sub>2</sub>, the  $\text{p-WS}_2$  pho-

Table II. Photoassisted Reduction of Ia at p-WS<sub>2</sub> and Platinized p-InP

photo-electrode	input power, mW (intensity, mW/cm <sup>2</sup> )	$E_V(\text{oc})$ , mV <sup>a</sup> ( $E_V$ at $\eta_{\text{max}}$ ) <sup>b</sup>	$\eta_{\text{max}}$ , % <sup>c</sup>	$\Phi_e$ at $E_{\text{redox}}$ <sup>d</sup>	FF <sup>e</sup>
platinized p-InP	0.02 (0.4)	500 (340)	5.8	0.53	0.43
	0.05 (1.0)	530 (340)	3.0	0.35	0.32
	0.25 (5.0)	570 (340)	0.7	0.08	0.30
p-WS <sub>2</sub>	0.10 (1.4)	620 (400)	1.6	0.18	0.28
	0.20 (2.8)	680 (400)	1.4	0.13	0.22
	0.50 (7.1)	740 (400)	0.9	0.08	0.33

<sup>a</sup> Photovoltage; onset of photocathodic current for reduction of ~4 mM Ia in 0.1 M KCl/pH 7.2 relative to  $E_{\text{redox}} = -0.4$  V vs. SCE. <sup>b</sup> Photovoltage at maximum power point; extent to which the photoelectrode potential is more positive than  $E_{\text{redox}} = -0.4$  V vs. SCE when the value of (photovoltage)  $\times$  (photocurrent) is maximum. <sup>c</sup>  $E_V$  at  $\eta_{\text{max}}$  times photocurrent at the maximum power point times 100% divided by input 632.8 nm power. <sup>d</sup> Quantum yield for electron flow when the photocathode is at  $E_{\text{redox}} = -0.4$  V vs. SCE. <sup>e</sup> FF is the fill factor;  $E_V$  at  $\eta_{\text{max}}$  times the photocurrent at the maximum power point divided by  $E_V(\text{oc})$  times the photocurrent at  $E_{\text{redox}}$ .

toassisted reduction of Ia in a solution poised to  $-0.40$  V vs. SCE has  $\eta_{\text{max}} \approx 2\%$ , well below the best values of  $\eta_{\text{max}}$  attained with p-WS<sub>2</sub>.<sup>2</sup> The best values of  $\eta_{\text{max}}$  for the p-WS<sub>2</sub> photocathodes are for solutions that are poised to more positive potentials.<sup>2</sup> We undertook an investigation of the photoassisted reduction of Ia at p-InP that gives good efficiencies for negative values of  $E_{\text{redox}}$ .<sup>3</sup> Unfortunately, the naked p-InP photocathode appears to suffer from a strong interaction with Ia that results in poor kinetics (Figure 8). However, platinized p-InP gives a significantly better response to Ia and gives a good efficiency for the sustained reduction of Ia in aqueous solution (Figure 8). Table II summarizes some output data for p-WS<sub>2</sub>- and p-InP-based cells for the photoassisted reduction of Ia. The  $\eta_{\text{max}}$  for p-InP for the reduction of Ia in solutions poised to  $-0.40$  V vs. SCE is significantly higher than for the p-WS<sub>2</sub>, owing to the better values for quantum yield and fill factor, despite the larger maximum photovoltage for the p-WS<sub>2</sub>. Note that p-InP photoassisted reduction of O<sub>2</sub> in solutions containing Ia cannot be sustained, owing to decomposition of the InP by H<sub>2</sub>O<sub>2</sub>. Additionally, reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> at Pt is not likely to have high current efficiency,<sup>14</sup> since O<sub>2</sub> could be reduced to H<sub>2</sub>O, the H<sub>2</sub>O<sub>2</sub> could be reduced, and the H<sub>2</sub>O<sub>2</sub> could be catalytically decomposed. Another problem with the p-InP is that the photovoltage relative to  $E^\circ(\text{O}_2/\text{H}_2\text{O}_2)$  is expected to be smaller than for p-WS<sub>2</sub>, based on data for redox couples having a similar  $E^\circ$ .<sup>2,15</sup>

To summarize the results from the photoassisted reductions, p-InP and p-WS<sub>2</sub> photocathodes can be used to effect the uphill reduction of a quinone to form a reduced species that quantitatively yields H<sub>2</sub>O<sub>2</sub> upon exposure to O<sub>2</sub>. In the case of p-WS<sub>2</sub> with Ia in solution, the reduction of O<sub>2</sub> can be effected with a photovoltage relative to  $E^\circ(\text{O}_2/\text{H}_2\text{O}_2)$  of up to 600 mV. The sustained photoassisted generation of H<sub>2</sub>O<sub>2</sub> at electrode potentials positive of  $E^\circ(\text{O}_2/\text{H}_2\text{O}_2)$  is possible, but overall energy conversion efficiency is low. Improvement in efficiency hinges on the ability to find a photocathode that has a more positive set of band edges so that

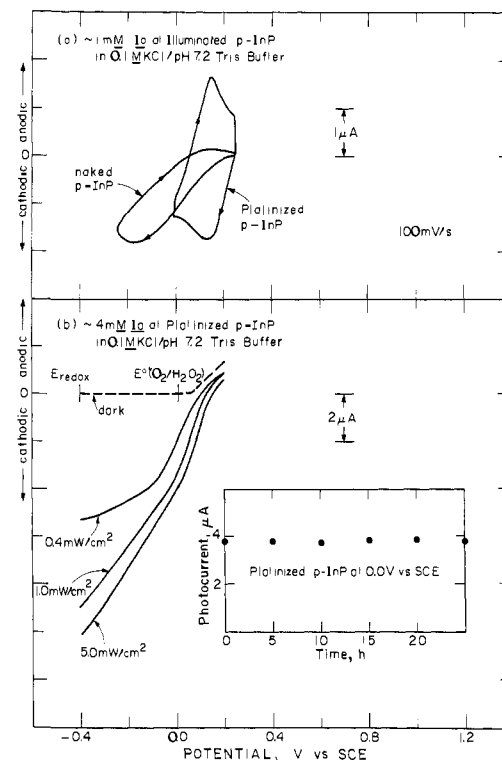


Figure 8. Cyclic voltammetry of Ia at naked and platinized ( $\sim 1 \times 10^{-7}$  mol/cm<sup>2</sup> Pt) p-InP illuminated with 632.8 nm light ( $\sim 40$  mW/cm<sup>2</sup>) (top). Steady-state photocurrent voltage curves for the reduction of Ia (bottom); cf. Table II. Inset shows plot of photocurrent vs. time for p-InP held at 0.0 V vs. SCE.

the photovoltage can be greater. This might necessitate the use of a quinone (or other mediator) having a more positive  $E^\circ$ . Studies are now in progress in this laboratory to optimize the quinone system.

### Summary

The naphthoquinones Ia and [Q]<sub>surf</sub> from Ib are useful solution and surface mediators, respectively, for the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. The rate of reaction of [QH<sub>2</sub>]<sub>surf</sub> with O<sub>2</sub> or with Ia is fast; the rate constant is no less than  $0.65 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  from rotating-disk electrode measurements. A significant rate for the redox equilibration of the solution and surface redox couples makes possible the electrochemical reduction of [M<sub>x</sub>O<sub>y</sub>]-[Q] via mediation by Ia. The synthesis of pure [M<sub>x</sub>O<sub>y</sub>]-[QH<sub>2</sub>] has allowed the generation of up to 0.1 M H<sub>2</sub>O<sub>2</sub> in pure H<sub>2</sub>O by reaction of [M<sub>x</sub>O<sub>y</sub>]-[QH<sub>2</sub>] with O<sub>2</sub>.

The photoassisted reduction of Ia and its use as a solution mediator to effect the overall reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> in an uphill sense has been demonstrated at illuminated p-WS<sub>2</sub>. The photoassisted reduction of Ia also evidences the ability to effect the photoassisted reduction of [M<sub>x</sub>O<sub>y</sub>]-[Q].

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**Registry No.** Ia, 83027-25-2; Ib, 83027-26-3; II, 64897-02-5; O<sub>2</sub>, 7782-44-7; H<sub>2</sub>O<sub>2</sub>, 7722-84-1; Al<sub>2</sub>O<sub>3</sub>, 1344-28-1; SiO<sub>2</sub>, 7631-86-9; WS<sub>2</sub>, 12138-09-9; Pt, 7440-06-4; BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>, 51826-90-5; n-PrBr, 106-94-5; InP, 22398-80-7; 2-chloro-3-[(2-(dimethylpropylammonio)ethylamino)-1,4-naphthalenediol], 86307-90-6; 2,3-dichloro-1,4-naphthoquinone, 117-80-6; N,N-dimethylethylenediamine, 108-00-9.

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