°C), $[\alpha]_D$ 30.4° (*c* 0.55, $CHCl_3$), which was identical in all respects with an authentic sample prepared in our laboratory by degradation of tylosin.[11,15]

Acknowledgment. This research was supported by a Public Health Research Grant from the National Institute of Allergy and Infectious Diseases (AI 17410). The 360-MHz NMR instrument (Nicolet) used in the above studies was purchased in part through funds provided by the National Science Foundation (Grant No. CHE-81-05004). We are grateful to Dr. Tats Matsuoka (Lilly Research Laboratories) and Dr. Arthur Nagel (Pfizer Central Research) for generous gifts of tylosin.

Supplementary Material Available: Spectral and analytical data for **1–3**, **5–8**, **10–19**, **22**, **24**, **25**, **27** (R = Me), and **28** (7 pages). Ordering information is given on any current masthead page.

(15) Assigned structures are fully supported by IR, NMR, and combustion analysis.

Application of Rapid-Scan Fourier Transform Infrared Spectroscopy To Characterize the Monodentate Intermediate in the Photochemical Formation of Tetracarbonyl(4,4'-dialkyl-2,2'-bipyridine)metal from Hexacarbonylmetal

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We report direct infrared spectral evidence establishing that the photochemical formation of $M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$ (M = Cr, Mo, W; R = CH_3, $n\text{-}C_{19}H_{39}$; bpy = bipyridine) from $M(CO)_6$ occurs via $M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$, where the potentially bidentate ligand is coordinated in a monodentate fashion (eq 1–3). This study was stimulated by the observation that

$$M(CO)_6 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} M(CO)_5 + CO \tag{1}$$

$$M(CO)_5 + 4,4'\text{-}R_2\text{-}2,2'\text{-bpy} \xrightarrow{\Delta,\ \text{fast}} M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) \tag{2}$$

$$M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) \xrightarrow{\Delta,\ k_3} M(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bpy}) + CO \tag{3}$$

$M(CO)_4L$ (L = bidentate ligand) could be generated in a one-photon process. The use of rapid-scan Fourier transform infrared (FT IR) spectroscopy, a complement to time-resolved Raman spectroscopy,[1] provides definitive, molecular specific characterization not typically obtained in the study of light-induced reactions monitored in the UV–vis region of the spectrum.

It is established that near-UV irradiation of $M(CO)_6$ (M = Cr, Mo, W) results in efficient ($\Phi > 0.1$) dissociative loss of CO, eq 1,[2] forming a 16-valence-electron $M(CO)_5$, which reacts readily with solvent to form a weakly bound solvent complex that can rapidly react with two-electron donor ligands such as pyridine with a second-order rate constant of $\sim 2 \times 10^6$ s^{-1}.[2b,c,e] Figure 1a shows the FT IR spectral changes observed within 5 s after ~2-s irradiation of a 0.5 mM $W(CO)_6$ solution in methylcyclohexane containing 0.3 mM 2-phenylpyridine and ~1 mM CO.[3] The negative peak at 1981 cm^{-1} corresponds to the disappearance of $W(CO)_6$, and positive peaks at 2070, 1930, and 1911 cm^{-1} correspond to the appearance of $W(CO)_5$(2-phenylpyridine). Nearly the same spectrum is observed for authentic samples of $W(CO)_5(py)$ (py = pyridine) (Table I). Figure 1b shows that similar FT IR spectral changes occur within 5 s after a 2-s irradiation of 0.5 mM $W(CO)_6$ in methylcyclohexane containing 8.7 mM $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}$[4] and ~1 mM CO, consistent with the formation of $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ (2066, 1925, 1909 cm^{-1}), where only one nitrogen is coordinated, since

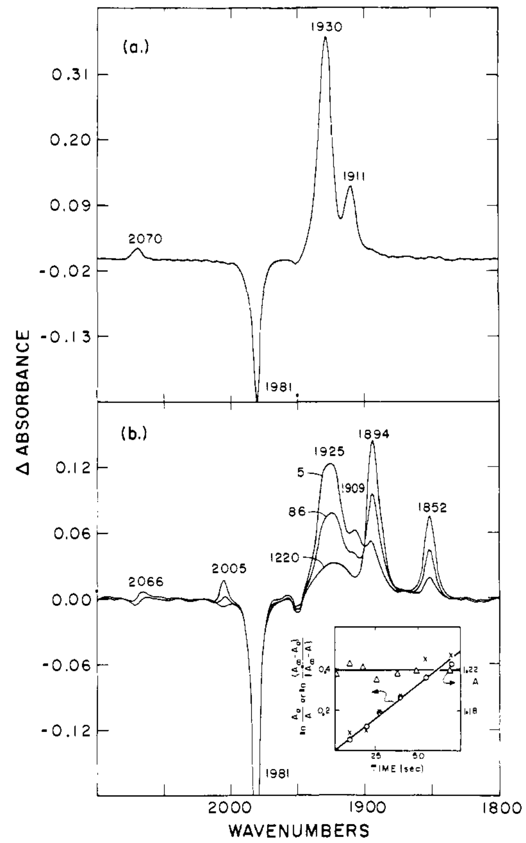

Figure 1. Infrared spectral changes resulting from irradiation of $W(CO)_6$. (a) Difference infrared spectrum obtained within 5 s after irradiation with a 200-W high-pressure Hg lamp of a 0.5 mM $W(CO)_6$ solution containing 6.3 mM 2-phenylpyridine, showing the disappearance of $W(CO)_6$ as a negative peak at 1981 cm^{-1} and appearance of $W(CO)_5$(2-phenylpyridine) as positive at 2070, 1930, and 1911 cm^{-1}. (b) Difference infrared spectra 5, 86, and 1220 s after irradiation with a 200-W high-pressure Hg lamp of a 0.5 mM $W(CO)_6$ solution containing 8.7 mM $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}$. Inset shows time-dependent behavior of peaks at 1981 cm^{-1} corresponding to $W(CO)_6$ (△), 1925 cm^{-1} corresponding to $W(CO)_5(4,4'\text{-}n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ (○), and 1894 cm^{-1} corresponding to $W(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ (×). The remaining absorbance at 1925 cm^{-1} after 1220 s is attributed to a monodentate ligand impurity. The presence of this peak is accounted for in the kinetic analysis.

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(1) Cf., for example: (a) Hub, W.; Schneider, S.; Dorr, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 323. (b) Atkinson, G. H.; Dosser, L. R. *J. Chem. Phys.* **1980**, *72*, 2195; (c) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1981**, *103*, 2495; (d) Dallinger, R. F.; Farquharson, S.; Woodruff, W. H.; Rogers, M. A. *Ibid.* **1981**, *103*, 7433; (e) Hub, W.; Schneider, S.; Dorr, F.; Simpson, J. T.; Oxman, J. D.; Lewis, F. D. *Ibid.* **1982**, *104*, 2044.

(2) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979, Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401; (b) Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1981**, *20*, 4381; (c) Tyler, D. R.; Petrylak, D. P. *J. Organomet. Chem.* **1981**, *212*, 389; (d) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791; (e) Bonneau, R.; Kelly, J. M. *Ibid.* **1980**, *102*, 1220.

(3) All reactions were carried out in deoxygenated, olefin-free methylcyclohexane solvent. Generally, solutions were 1 mM in CO to allow in situ monitoring of the importance of $M(CO)_5S \rightarrow M(CO)_6$ during the short time scale experiments. Samples were loaded into 0.1-mm path length cells under CO. Irradiation of the sample in the cell was carried out for a brief period at 298 K, and the sample was transferred as rapidly as possible to the Nicolet 7199 FT IR to record FT IR spectra every ~0.2 s to follow the reaction.

(4) Obtained as a gift from S. J. Valenty (lab notebook no. 10900-50-2) of General Electric Research and Development Center, Schenectady, NY. The long alkyl chain derivative was used since $M(CO)_4(2,2'\text{-bpy})$ precipitates upon formation in alkane solvents.

0002-7863/82/1504-5784$01.25/0

Table I. Infrared Spectral Data for Relevant Complexes[a]

compound	IR, $\mathrm{cm^{-1}}$ (rel abs)
$W(CO)_6$	1981
$W(CO)_5(py)$	2071 (w), 1930 (s), 1918 (m)[b]
$W(CO)_5$(2-phenylpyridine)	2070 (1.0), 1930 (17.0), 1911 (5.5)
$W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$	2066 (1.0), 1925 (20.0), 1909 (8.0)
$W(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$	2005 (1.0), 1894 (1.8), 1852 (1.0)
$W(CO)_5(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bpy})$	2070 (1.0), 1926 (15.3), 1908 (4.7)
$W(CO)_4(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bpy})$	2007 (1.0), 1897 (2.8), 1847 (1.9)
$W(CO)_4(4,7\text{-}Ph_2\text{-}1,10\text{-phen})$	2006 (1.0), 1898 (3.2), 1855 (1.6)
$Mo(CO)_6$	1987
$Mo(CO)_5$(2-phenylpyridine)	2071 (1.0), 1940 (25.7), 1912 (8.5)
$Mo(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$	2012 (1.0), 1905 (5.0), 1893 (sh, 2.0), 1855 (2.7)
$Cr(CO)_6$	1986
$Cr(CO)_5$(2-phenylpyridine)	2066 (1.0), 1936 (15.0), 1912 (6.0)
$Cr(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$	2069 (1.0), 1925 (11.2), ~1915 (4.3)
$Cr(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$	2008 (1.0), 1905 (8.3), 1895 (sh, 4.6), 1849 (4.2)

[a] All spectra obtained in methylcyclohexane solution at 298 K. [b] Data in isooctane solution taken from Wrighton et al. (Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105); (w) = weak, (s) = strong, (m) = medium.

the infrared spectrum in the carbonyl stretching region is very similar in position and relative intensities to that observed for $W(CO)_5$(2-phenylpyridine) (Table I).

Infrared spectral features associated with $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ decline with a first-order rate constant of $6.8 \pm 0.8 \times 10^{-3}\ \mathrm{s^{-1}}$ (raw data shown in inset in Figure 1b), and concomitantly new infrared spectral features grow in at 2005, 1894, and 1852 $\mathrm{cm^{-1}}$ with a first-order rate constant of $6.8 \pm 1.8 \times 10^{-3}\ \mathrm{s^{-1}}$ as shown by monitoring the infrared spectral changes as a function of time with rapid-scan FT IR (Figure 1b). These new infrared bands are assigned to $W(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ based on FT IR spectral comparison with authentic samples of $W(CO)_4(2,2'\text{-bpy})$ derivatives (Table I) and comparison with optical spectra for such species.[5] The rate of this transformation is independent of $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy concentration over the range 1–9 mM (Table II) and is first order in $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$.

The lack of rate dependence on the concentration of $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy allows us to conclude that the 2066-, 1925-, and 1909-$\mathrm{cm^{-1}}$ features are not due to $W(CO)_5X$, where X is a solvent impurity with the rate-limiting step involving X dissociation, since the proportion of $W(CO)_5$ trapped by an impurity ligand would vary with changes in concentration of the deliberately added ligand. Also, the 2066-, 1925-, and 1909-$\mathrm{cm^{-1}}$ features cannot be attributed to $M(CO)_5$(solvent) for two reasons. First, irradiation in the absence of the 2,2′-bpy, but with 1 mM CO, yields no long-lived FT IR detectable species. Second, the infrared spectrum of $M(CO)_5$(methylcyclohexane) is different[2c] than what we observe for $M(CO)_5(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$. Further, the absence of any appreciable $W(CO)_6$ regeneration even in the presence of ~1 mM CO establishes that the $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ species is not labile with respect to $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy loss, since any $W(CO)_5$ thus formed could be competitively scavenged by CO. Thus, we can conclude that spectral changes in Figure 1b are those associated with eq 1–3 and that the rates measured in the dark following irradiation give the rate constant, k_3. The measured rate of $\sim 6 \times 10^{-3}\ \mathrm{s^{-1}}$ at 298 K corresponds to a half-life of ~100 s; by comparison the rate for thermal dissociative loss of CO from $W(CO)_6$ is $10^{-14}\ \mathrm{s^{-1}}$ and has an activation enthalpy of 39.9 kcal/mol.[6] Further, the $M(CO)_5(py)$ complexes are relatively thermally inert with respect to formation of $M(CO)_4(py)_2$. The significant increase in rate of CO loss in $W(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ is likely due to an overwhelming contribution from the associative ligand replacement reaction,[7] since the monodentate $4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy is locked into the coordination sphere. Similar results are obtained with $4,4'\text{-}(CH_3)_2\text{-}2,2'$-bpy (Table II).

Table II. Measured Rate Constants for Conversion of Monodentate to Bidentate Ligand Coordination[a]

		k_3, $\mathrm{s^{-1}}$	
ligand (concn, mM)	metal	disappearance of $M(CO)_5L$	appearance of $M(CO)_4L$
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy (1.3)	W	$(5.3 \pm 3.0) \times 10^{-3}$	$(6.7 \pm 1.8) \times 10^{-3}$
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy (4.5)	W	$(5.4 \pm 0.8) \times 10^{-3}$	$(6.1 \pm 2.1) \times 10^{-3}$
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2$-bpy (8.7)	W	$(6.8 \pm 0.8) \times 10^{-3}$	$(6.8 \pm 1.8) \times 10^{-3}$
$4,4'\text{-}(CH_3)_2\text{-}2,2'$-bpy (6.8)	W	$(7.6 \pm 3.0) \times 10^{-3}$	$(5.7 \pm 1.5) \times 10^{-3}$
$4,7\text{-}Ph_2\text{-}1,10$-phen (~2)	W	$>2 \times 10^{-2}$	
2-phenylpyridine (6.3)	W	$<4 \times 10^{-5}$	
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy (3.6)	Mo	$>2 \times 10^{-2}$	
2-phenylpyridine (6.3)	Mo	$(2.7 \pm 1.0) \times 10^{-4}$ [b]	
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy (2.0)	Cr	$(3.1 \pm 2.5) \times 10^{-3}$	$(6.8 \pm 1.2) \times 10^{-3}$
$4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'$-bpy (4.6)	Cr	$(8.1 \pm 2.7) \times 10^{-3}$	$(8.9 \pm 1.9) \times 10^{-3}$
2-phenylpyridine (6.3)	Cr	$(3.3 \pm 1.0) \times 10^{-4}$ [b]	

[a] All measurements were done at 298 K in deoxygenated methylcyclohexane solutions containing ~1 mM CO and 0.5–1.0 mM $M(CO)_6$. Solutions were irradiated with a Bausch and Lomb 200-W high-pressure Hg lamp for ~2 s and then placed in the Nicolet 7199 FT IR, where the infrared spectra were monitored as a function of time. [b] Regeneration of $M(CO)_6$ occurs concomitantly with the disappearance of $M(CO)_5$(2-phenylpyridine) with a pseudo-first-order rate constant of $(2.4 \pm 0.6) \times 10^{-4}\ \mathrm{s^{-1}}$ (M = Cr) or $(3.3 \pm 1.0) \times 10^{-4}\ \mathrm{s^{-1}}$ (M = Mo).

In contrast to experiments with $4,4'\text{-}R_2\text{-}2,2'$-bpy, irradiation of $W(CO)_6$ in the presence of 4,7-diphenyl-1,10-phenanthroline ($4,7\text{-}Ph_2\text{-}1,10$-phen) does not yield FT IR detectable intermediates on the 5-s time scale, giving a lower limit of $2 \times 10^{-2}\ \mathrm{s^{-1}}$ for k_4 (eq (4). This difference of at least a factor of 50 for the 1,10-phen

$$[W(CO)_5(4,7\text{-}Ph_2\text{-}1,10\text{-phen})] \xrightarrow{\Delta,\,k_4} CO + W(CO)_4(4,7\text{-}Ph_2\text{-}1,10\text{-phen}) \quad (4)$$

vs. 2,2′-bpy in rate is due to the rigid nature of the 1,10-phen ring system, where the nitrogens are constrained to always be on the same side and coplanar in contrast to the possible rotation about the C_2–$C_2{}'$ bond in 2,2′-bpy. The presence of the large alkyl chains on the bipyridine derivative used does not significantly alter the rate of CO displacement, since $4,4'\text{-}(CH_3)_2\text{-}2,2'$-bpy reacts at approximately the same rate (Table II).

The rate constant for CO displacement from $Mo(CO)_5(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ is at least 50 times faster than the corresponding W species, while the Cr species reacts at approximately the same rate (Table II). The Mo rate is deduced from the lack of FT IR detectable intermediates in the formation of $Mo(CO)_4(4,4'\text{-}R_2\text{-}2,2'\text{-bpy})$. This ordering of reactivity, Mo > W ≈ Cr, is consistent with the known thermal labilities for the hexacarbonyls of this triad.[6,7] The $M(CO)_5$(2-phenylpyridine) (M = Mo, Cr) complexes are somewhat labile with respect to loss of 2-phenylpyridine as shown by the regeneration of $M(CO)_6$. However, the rate for this process is slow ($\sim 3 \times 10^{-4}\ \mathrm{s^{-1}}$) relative to $M(CO)_4(4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy})$ formation and does not alter our conclusions.

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(6) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.

(7) Darensbourg, D. J. *Adv. Organomet. Chem.*, in press.

In summary, we have directly established the sequence represented by eq 1-3 for the photochemical formation of $M(CO)_4L$ from $M(CO)_6$ where L is a bidentate ligand. The use of rapid-scan FT IR allows molecular specific monitoring of a photochemically generated intermediate during its thermal reaction to form an isolable product. Importantly, the rate of the monodentate to bidentate conversion, eq 3, is an example of a low activation energy process that can be studied owing to the use of light to initially extrude CO from $M(CO)_6$. Dissociative loss of CO would be the rate-determining step in the thermal formation of $M(CO)_4L$ from $M(CO)_6$ precluding the study of reaction 3, a lower activation process. Future studies will be aimed at employing vibrational spectroscopic techniques described here to study reactions involving shorter lived intermediates.

Acknowledgment. We thank the National Science Foundation for support of this research and acknowledge support from the National Institutes of Health (Grant GM 27551) for the Nicolet 7199 FT IR used in these studies.

Registry No. $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; 4,4′-Me_2-2,2′-bpy, 1134-35-6; 4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 70268-37-0; $W(CO)_5$(2-phenylpyridine), 83005-91-8; $W(CO)_5$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 83005-92-9; $W(CO)_4$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy, 83005-93-0; $W(CO)_5$(4,4′-$(CH_3)_2$-2,2′-bpy), 83005-94-1; $W(CO)_4$-(4,4′-$(CH_3)_2$-2,2′-bpy), 26546-43-0; $W(CO)_4$(4,7-Ph_2-1,10-phen), 83005-95-2; $Mo(CO)_5$(2-phenylpyridine), 83005-96-3; $Mo(CO)_4$(4,4′-(n-$C_{19}H_{39}$)-2,2′-bpy), 83005-97-4; $Cr(CO)_5$(2-phenylpyridine), 83005-98-5; $Cr(CO)_5$(4,4′-(n-$C_{19}H_{39})_2$-2,2′-bpy), 83005-99-6; $Cr(CO)_4$(4,4′-(n-$C_{19}H_{39}$)-2,2′-bpy), 83006-00-7.

Electrochemical Behavior of a Surface-Confined Naphthoquinone Derivative. Electrochemical and Photoelectrochemical Reduction of Oxygen to Hydrogen Peroxide at Derivatized Electrodes

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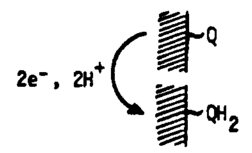
We describe the synthesis and application of a naphthoquinone reagent, I, that can be used to catalyze the reduction of O_2 to H_2O_2 at conventional electrodes or at illuminated p-type semiconducting photoelectrodes. Direct reduction of O_2 in aqueous solution to form H_2O_2, without H_2O formation and near the thermodynamic potential, does not occur readily at electrodes.[1] Much work has been directed to the catalysis of O_2 reduction at electrodes by using metal macrocycle complexes,[1a,2] but in all cases it would appear that H_2O_2, or radicals from the formation or the decomposition of H_2O_2, leads to degradation of the electrocatalyst. We were prompted to study the quinone systems, since eq 1 and 2 represent

$$Q \xrightarrow[\text{catalyst}]{H_2,\ \Delta} QH_2 \tag{1}$$

$$QH_2 + O_2 \xrightarrow{\Delta} Q + H_2O_2 \tag{2}$$

a viable pathway to the large-scale synthesis of H_2O_2,[3] where Q is a 9,10-anthraquinone derivative and QH_2 is the corresponding dihydroxy species. The electrochemical approach described here is represented by Scheme I[4,5] and the issues of concern are the (i) electrochemical potential, kinetics, and durability of the $[Q/QH_2]_{\text{surf.}}$ couple, (ii) rate of reaction of O_2 with $[QH_2]_{\text{surf.}}$, and (iii) behavior of the $[Q/QH_2]_{\text{surf.}}$ in the presence of H_2O_2. An advantage with the electrochemical synthesis of H_2O_2 is that H_2 need not be involved, and the potential necessary to reduce O_2 is 0.68 V less reducing than needed to produce H_2.

Scheme I



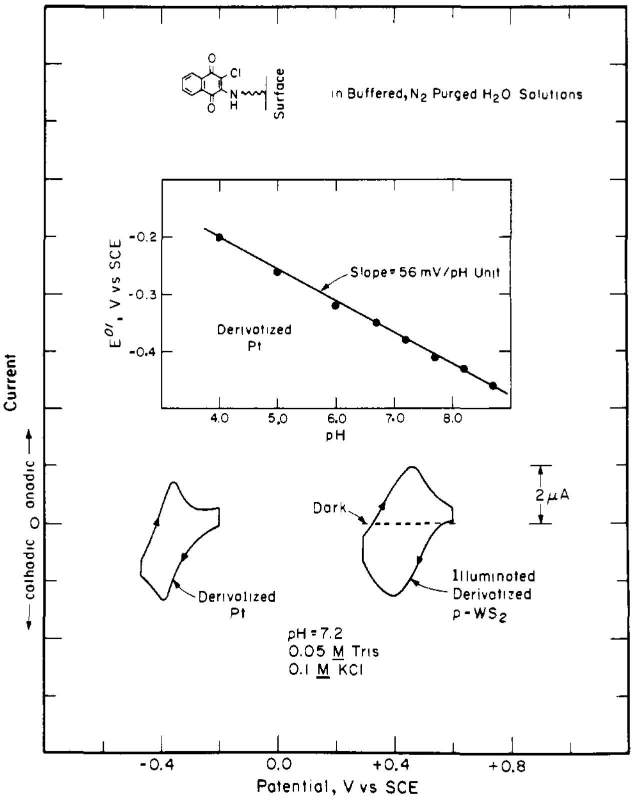


Figure 1. Cyclic voltammetry (100 mV/s) of Pt or illuminated p-WS_2 (632.8 nm, ~40 mW/cm^2) derivatized with Ib. Coverage (from integration of cyclic waves) in both cases is $\sim 10^{-10}$ mol/cm^2 of the $[Q/QH_2]_{\text{surf.}}$ system. The inset shows $E°'[Q/QH_2]_{\text{surf.}}$ on Pt as a function of pH.

The synthesis of reagent I was achieved by the chemistry represented in eq 3 and 4,[6] beginning with a commercially available (Aldrich) quinone. Reagent Ib bears a $Si(OMe)_3$ group that is

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(4) A patent describes a similar objective using a "polyquinone" formed from benzoquinone, phenol, and formaldehyde adsorbed onto graphite electrodes: Grangaard, D. H., U.S. Patent 3 454 477, 1969.

(5) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. See the following for use of electrodes bearing quinone functionality: (a) Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5728; *J. Electroanal. Chem.* **1981**, *117*, 267. (b) Fukui, M.; Kitani, A.; Degrand, C.; Miller, L. L. *J. Am. Chem. Soc.* **1982**, *104*, 28. (c) Ueda, C.; Tse, D. C.-S.; Kuwana, T. *Anal. Chem.* **1982**, *54*, 850. (d) Tse, D. C.-S.; Kuwana, T. *Ibid.* **1978**, *50*, 1315.

(6) The HCl salt of 2-chloro-3-[[2-(dimethylamino)ethyl]amino]-1,4-naphthoquinone was prepared by the method of Cheng, C. C.; et al. *J. Med. Chem.* **1979**, *22*, 501. The free base was then prepared by treating the HCl salt with excess aqueous Na_2CO_3, followed by extraction into CH_2Cl. The solution was then dried over $MgSO_4$ and filtered and the CH_2Cl_2 was removed under vacuum. Ib was prepared by stirring 1 g of the free base in 5 mL of $BrCH_2CH_2CH_2Si(OCH_3)_3$ [prepared by reacting $HC(OCH_3)_3$ with 1-bromo-3-(trichlorosilyl)propane purchased from Petrarch Chemical Co.] at 90 °C for 12 h, after which time the product had precipitated from the solution. Filtration and repeated washings with hexane followed by drying under vacuum yileded 1.6 g (~90%) of Ib. Ia was prepared in an analogous manner by stirring the free base with n-PrBr.

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