Contribution from the Kenan Laboratories of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Electron Exchange in Photodeposition of Poly(vinylferrocene) on Platinum Electrodes from Methylene Chloride Solutions

D. R. ROLISON, M. UMAÑA, P. BURGMAYER, and ROYCE W. MURRAY*

Received October 6, 1980

Electrochemically reactive films of poly(vinylferrocene) on Pt can be obtained by spontaneous adsorption of polymer from CH_2Cl_2 solution and, more rapidly, by concurrent ultraviolet irradiation of the CH_2Cl_2 solution. Although photooxidation of dissolved polymer, to ferrocenium, is extensive, the film deposited on Pt from the photolyzed solution is, by XPS, exclusively in the reduced, poly(vinylferrocene) state. Ferrocenium sites become reduced because of a difference in the formal electrochemical potentials of surface and dissolved polymer. Data on cyclic voltammetric properties and on stability characteristics of the polymer films are presented.

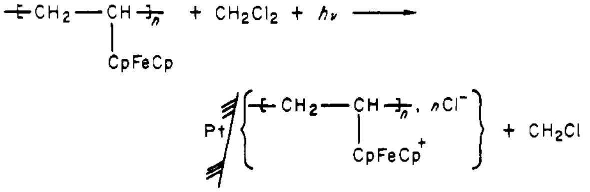
Much of the recent work on chemically modified electrodes has involved coating electrodes with thin films of polymers[1-10] which contain fixed, electroactive sites, i.e., redox polymers. Unlike monomolecular electrode modification strategies,[11-13] redox polymer films do not demand covalent bonding to the electrode surface and can rely on adsorptive adherance to the electrode and/or low solubility in the contacting solvent. Procedures for coating electrodes have included dip coating, spin coating, droplet evaporation,[1-8] and electrochemical precipitation[9] from solutions of formed polymers and in situ polymerization coating using radio frequency plasmas.[7,8,10]

In the course of coating Pt electrodes by droplet evaporation of poly(vinylferrocene) solutions, for comparison of their electrochemical behavior with that of RF plasma polymerized vinylferrocene,[8] we discovered that, under ambient illumination, photolytic oxidation of poly(vinylferrocene) occurs during solvent evaporation when the solvent employed is methylene chloride.[7] X-ray photoelectron spectroscopy (XPS) shows a ferrocenium Fe $2p_{3/2}$ band in this case, at 711.2 ev, whereas films prepared by evaporation of toluene solutions, or from CH_2Cl_2 solutions in the dark, show only the reduced ferrocene peak of poly(vinylferrocene), at 709 ev. Ferrocene is known[14-16] to become photooxidized in chlorinated solvents via a charge-transfer band at 325 nm (eq 1). This reaction

$$Cp_2Fe + CH_2Cl_2 \xrightarrow{h\nu} [Cp_2Fe\cdots CH_2Cl_2]^* \rightarrow Cp_2Fe^+ + Cl^- + CH_2Cl\cdot \quad (1)$$

is useful for free-radical photoinitiations.[16,17] From our results it also occurs in CH_2Cl_2 solutions of poly(vinylferrocene).

Following observations by Smith et al.[18] and Merz and Bard[9a] that poly(vinylferrocene), when electrochemically oxidized in CH_2Cl_2 solvent, tends to coat the electrode, it occurred to us that oxidation via reaction 1 should also lead to electrode coatings. No photochemical procedures have been reported for making redox polymer films. The proposed reaction was



$$\text{-}[CH_2-CH]_n\text{-}(CpFeCp) + CH_2Cl_2 + h\nu \longrightarrow Pt/\{\text{-}[CH_2-CH]_n\text{-}(CpFeCp^+),\ nCl^-\} + CH_2Cl \quad (2)$$

We describe here the photolysis of poly(vinylferrocene) in CH_2Cl_2 solvent in contact with Pt. Electrode coating, or photodeposition, indeed occurs, but reaction 2 oversimplifies events, since photodeposition yields a *reduced*, not oxidized, film of poly(vinylferrocene).

Experimental Section

Chemicals. Two samples of poly(vinylferrocene) were used. One was prepared from (sublimed) monomer according to a procedure[18] yielding an average $M_r = 26000$. Anal. Calcd: C, 67.96; H, 5.70; Fe, 26.34. Found (Galbraith Laboratories): C, 65.11; H, 5.88; Fe, 25.10. Another sample of apparently somewhat lower molecular weight was a gift from Professor M. S. Wrighton (MIT); this sample gave the analysis % C (found) = 66.71 and % H (found) = 5.76. Both samples give distinct 708.5-eV XPS bands for ferrocene Fe $2p_{3/2}$.

Vinylferrocene was obtained from Pfaltz and Bauer; $LiClO_4$, $NaClO_4$, and n-Bu_4NClO_4 were used as received from G. F. Smith. Et_4NClO_4 (Eastman) was thrice recrystallized from water, and

---

[1] (a) Van De Mark, M. R.; Miller, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 3223. (b) Kerr, J. B.; Miller, L. L. *J. Electroanal. Chem.* **1979**, *101*, 263. (c) Kerr, J. B.; Miller, L. L.; Van De Mark, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 3383.

[2] Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 739, 3450.

[3] Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 640.

[4] Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980**, *127*, 247, 249.

[5] (a) Kaufman, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chamgers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483. (b) Kaufman, F. B.; Engler, E. M. *J. Am. Chem. Soc.* **1979**, *101*, 547.

[6] (a) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadjo, L.; Palazzotto, M. C. *J. Electroanal. Chem.* **1978**, *87*, 429; (b) Wrighton, M. S.; Austin, R. G.; Bocarsly, A. B.; Bolts, J. M.; Haas, O.; Legg, K. D.; Nadio, L.; Palazzotto, M. C. *J. Am. Chem. Soc.* **1978**, *100*, 1602. (c) Bolts, J. M.; Wrighton, M. S.; *Ibid.* **1978**, *100*, 5257. (d) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *Ibid.* **1979**, *101*, 1378. (e) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *Ibid.* **1978**, *100*, 7264. (f) Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal Chem.* **1979**, *100*, 283. (g) Bocarsly, A. B.; Walton, E. G.% Wrighton, M. S. *J. Am. Chem. soc.* **1980**, *102*, 3390. (h) Bookbinder, D. C.; Wrighton, M. S. *Ibid.* **1980**, *102*, 5123.

[7] Umaña, M.; Rolison, D. R.; Nowak, R. J.; Daum, P.; Murray, R. W. *Surf. Sci.* **1980**, *101*, 295. Umaña, M.; Rolison, D. R.; Nowak, R. J.; Daum, P.; Murray, R. W. In "Non-Traditional Approaches to the Solid-Electrolyte Interface"; Furtak, T. E., Kliewer, K. L.; Lynch, D. W., Eds.; North-Holland Publishing Co.: Amsterdam, 1980; p 295.

[8] Daum, P. H.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389.

[9] (a) Merz, A.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 3222. (b) Itaya, K.; Bard, A. J. *Anal. Chem.* **1978**, *50*, 1487. (c) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *108*, 121.

[10] (a) Nowak, R.; Schultz, F. A.; Umaña, M.; Abruña, H.; Murray, R. W. *J. Electroanal. Chem.* **1978**, *94*, 219. (b) Nowak, R. J.; Schultz, F. A.; Umaña, M.; Lam, R.; Murray, R. W. *Anal. Chem.* **1980**, *52*, 315. (c) Daum, P.; Murray, R. W. *J. Electroanal. Chem.* **1979**, *103*, 289. (d) Daum, P.; Lenhard, J. R.; Rolison, D. R.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4649. (e) Willman, K. W.; Rocklin, R. D.; Nowak, R.; Kuo, K.; Schultz, F. A.; Murray, R. W. *Ibid.* **1980**, *102*, 7629.

[11] Moses, P. R.; Wier, L.; Murray, R. W. *Anal. Chem.* **1975**, *47*, 1882.

[12] Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. *J. Am. Chem. Soc.* **1975**, *97*, 3549.

[13] Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.

[14] Brand, J. C. D.; Snedden, W. *Trans. Faraday Soc.* **1957**, *53*, 894.

[15] Akiyama, T.; Hoshi, Y.; Goto, S.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1851, 1855.

[16] Traverso, O.; Scandola, F. *Inorg. Chim. Acta* **1970**, *4*, 493.

[17] Traverso, O.; Scandola, F.; Carassiti, V. *Inorg. Chim. Acta* **1972**, *6*, 471.

[18] Smith, T. W.; Kuder, J. E.; Wycheck, D. *J. Polym. Sci.* **1976**, *14*, 2433.

0020-1669/81/1320-2996$01.25/0

Table I. Electrochemical Coverages and XPS on Pt Electrodes Exposed to CH_2Cl_2 Solutions of Poly(vinylferrocene)

			XPS BE, eV		
				evap soln	
expt	exposure conditions[a,b]	electrochemical Γ, mol/cm²	exposed electrode Fe $2p_{3/2}$	Fe $2p_{3/2}$	Cl $2p_{3/2}$
1	5.2 h UV, 5 mM PVF, 0.1 M n-Bu_4NClO_4	2.2×10^{-8}	708.6	*d*	
2	same as expt 1 except dark	0.62×10^{-8}	708.4	*d*	*d*
3	15 h UV, 5 mM PVF	3.6×10^{-8}	708.8	708.5, 711.8	198.8
4	40 h UV, 5 mM PVF	2.0×10^{-8}	708.8	708.5, 711.8	198.7
5	7 days ambient $h\nu$, 85 mM PVF	2.6×10^{-8}	709.0	712.4	*d*
6	same as expt 5 except dark	4.8×10^{-8}	708.7	708.8	*d*
7	1 h UV, 5 mM PVF, 0.1 M n-Bu_4NClO_4	2.4×10^{-8}			
8	same as expt 7 except dark	3.6×10^{-8}			
9	1.7 h UV, 5 mM PVF, 0.1 M n-Bu_4NClO_4, SiO_2 substrate		708.6	*d*	
10	2 h UV, 5 mM PVF			708.6, 711.9	198.6
11	expose evaporated film from expt 10 to photolyzed soln for 1 h			708.8	*d*
12	15 h UV, 47 mM vinylferrocene monomer	6.4×10^{-9}	708.8, 712.4 (198.7)[c]	708.6, 712.3	199.0

[a] PVF concentrations expressed in concentration of ferrocene sites. [b] All except experiments 7 and 8 used lower molecular weight PVF sample obtained from Professor M. S. Wrighton; experiments 7 and 8 used 26K prepared PVF. [c] Cl $2p_{3/2}$ BE. [d] Not determined.

acetonitrile (MCB Spectrograde) was dried and stored over molecular sieves.

Electrodes and Procedure. Pt foil (degreased in the solvents CH_3OH, hexane, and CH_2Cl_2) was placed in stoppered 1-cm quartz cuvettes under the poly(vinylferrocene) solution (1 mL) in CH_2Cl_2. The photolysis solution also contained 0.1 M n-Bu_4NClO_4 in certain experiments. No special efforts were made to exclude oxygen. Some experiments relied upon ambient, windowsill irradiation; most involved a low-power source with output centered at 255 nm (UV Product Mineralight UVS-11). Polymer solution concentrations are expressed in terms of ferrocene units.

The duration of photolysis was adjusted to impart at least a greenish cast to the originally yellow solution; most experiments were extended to yield a definite green product solution, which indicates extensive photooxidation to ferrocenium. A dark green precipitate begins to form thereafter; photolysis was (ordinarily) terminated before this stage. Following photolysis, the Pt foils were washed copiously with CH_3OH to circumvent evaporative deposition of residual polymer-CH_2Cl_2 solution and were used for electrochemical or XPS experiments. In one experiment, a $^1/_4$-in. silica disk was substituted for the Pt foil substrate.

Control (dark) experiments were conducted in identical fashion but without illumination.

Pt disk electrodes were coated with a film of photooxidized poly(vinylferrocene) by carefully spreading a droplet of its green CH_2Cl_2 solution after photolysis on the electrode and allowing the CH_2Cl_2 solvent to evaporate.

Measurements. Electrochemical experiments were performed with a PAR Model 173 potentiostat, in a cell of conventional design with a Pt auxillary electrode and Luggin probe to NaCl-saturated calomel electrode (SSCE).

X-ray photoelectron spectra (XPS) were obtained on a Du Pont Model 650B electron spectrometer, equipped with Mg anode and microprocessor unit for data acquisition and storage. Angular emission distributions were determined with a PHI Model 548AR electron spectrometer equipped with a movable slit. Binding energies are referenced to C 1s taken as 285.0 eV.

Results and Discussion

Cyclic Voltammetry of Photodeposited and Dark Adsorbed Poly(vinylferrocene). After photolysis of poly(vinylferrocene) solutions in contact with Pt, the Pt foils yield cyclic voltammetry typified by Figure 1A,C (experiment 1). This sample was prepared by a 5.2-h photolysis of 5 mM poly(vinylferrocene) solution in CH_2Cl_2 containing 0.1 M n-Bu_4NClO_4. CH_3CN employed for the cyclic voltammetry contains 0.1 M Et_4NClO_4 or Bu_4NClO_4 supporting electrolyte but no dissolved ferrocene reactant. The voltammetric peaks in Figure 1A thus correspond to the oxidation and rereduction of ferrocene sites in a polymer film clinging to the Pt surface. The formal potential (average of anodic and cathodic peak potentials), $E^\circ_{surf}{}' = 0.38$ V vs. SSCE, agrees with that (0.35 V) of a film of evaporatively deposited (dark) poly(vinylferrocene). The charge under the cyclic voltammetric peaks shows that $\Gamma = 2.2 \times 10^{-8}$ mol/cm² of ferrocene sites react in this film. Taking a monolayer of ferrocene sites as ca. 3×10^{-10} mol/cm², the Figure 1A voltammogram corresponds to the reaction of ca. 74 monolayer equivalents of ferrocene sites.

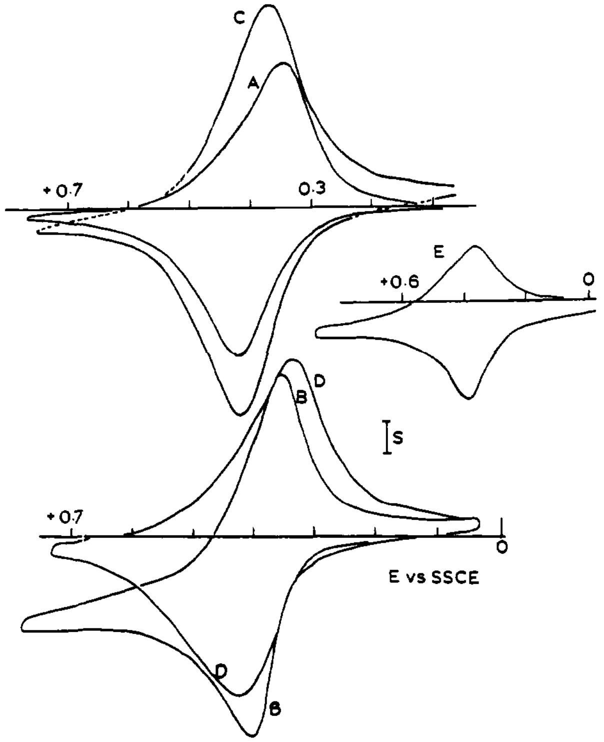


Figure 1. Cyclic voltammetry of films of poly(vinylferrocene) which have been photodeposited (curves A and C, experiment 1) from CH_2Cl_2 solution, adsorbed in the dark (curves B and D, experiment 2) from CH_2Cl_2 solution, and prepared by evaporation of droplet of photolyzed solution (curve E, from solution in experiment 1). Data are as follows [curve, electrolyte/solvent, scan rate (mV/s), S (μA/cm²), $E^\circ_{surf}{}'$ (mV), ΔE_p (mV), E_{fwhm} (anodic/cathodic) (mV)]: A, 0.1 M Et_4NClO_4/CH_3CN, 50, 142, +0.38, 100, 140/135; B, 0.1 M Et_4NClO_4/CH_3CN, 50, 42, +0.38, 48, 145/112; C, 0.1 M Bu_4NClO_4/CH_3CN, 50, 120, +0.39, 52, 132/124; D, 0.1 M Bu_4NClO_4/CH_2Cl_2, 200, 133, +0.38, 76, 113/165; E, 0.1 M Bu_4NClO_4/CH_3CN, 50, 28, +0.39, 20, 82/98.

Attained coverages of deposited polymer under various other conditions are given in Table I. Experiment 2 shows that exposure of a Pt foil to 5 mM poly(vinylferrocene) solution

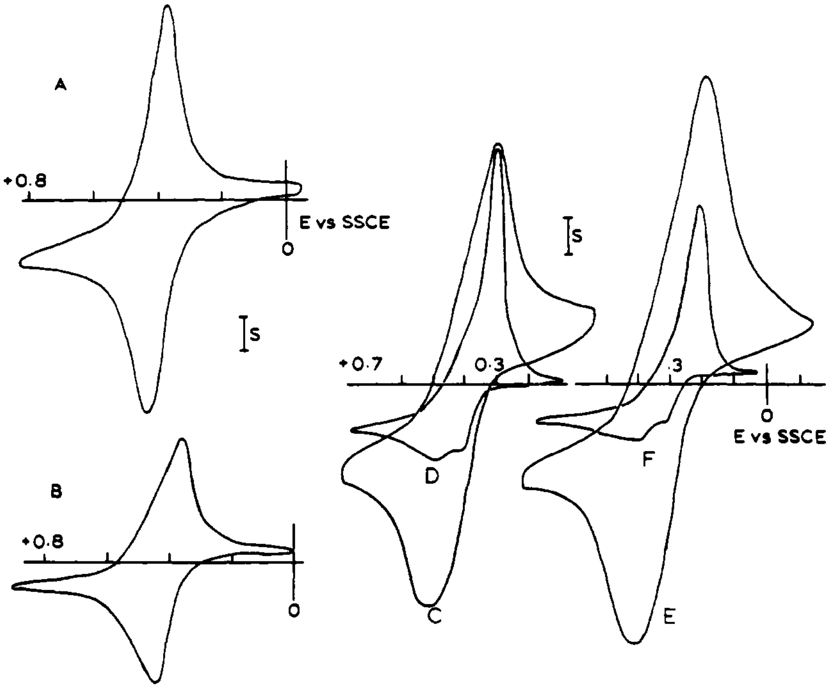


Figure 2. Cyclic voltammetry of films of 26K poly(vinylferrocene) which have been photodeposited (curve A, experiment 7) and adsorbed in the dark [curve B, experiment 8 (S = 50 μA/cm^2)] from CH_2Cl_2 solution, in 0.1 M Et_4NClO_4/CH_3CN at 50 mV/s and S = 48 μA/cm^2; cyclic voltammetry of solutions of polyvinylferrocene in 0.1 M Bu_4NClO_4/CH_2Cl_2, at freshly polished Pt, before photolysis (curve C, 100 mV/s; curve D, 5 mV/s, S = 5 μA/cm^2) and after photolysis (curve E, 100 mV/s; Curve F, 5 mV/s; S = 15 μA/cm^2, experiment 9).

for 5.2 h, in the dark, also yields a film of polyvinylferrocene on the Pt surface, with similar electrochemistry (Figure 1B) but with a surface coverage, $\Gamma = 6.2 \times 10^{-9}$ mol/cm^2, four times smaller than the photolysis result.

Coating of the Pt in the dark (Figure 1B) must be ascribed to spontaneous adsorption of the polymer from CH_2Cl_2 solution. Adventitious precipitation–evaporation effects associated with removal of the Pt foil from the polymer solution and rinsing were ruled out by procedural checks. Spontaneous adsorption from polymer solutions has been the basis for other electrode-coating experiments[1-4] but was not reported in previous studies of poly(vinylferrocene)/CH_2Cl_2 solutions.[9a,18] Photolysis of the poly(vinylferrocene) solution is thus not essential for film formation, but the larger coverage obtained with illumination shows that photolysis accelerates accumulation of the polymer on the Pt surface.

Reaction 2 involves charge separation and as such might logically be influenced by the ionic content of the solvent. On this basis, experiment 1 included 0.1 M n-Bu_4ClO_4 in the photolyzed solution. Photolysis carried out without electrolyte (experiment 3) proceeds qualitatively more slowly, 15 h being required to produce roughly the same solution color change (pale yellow ferrocene to pale green ferrocenium) as 5.2 h achieved in experiment 1. The electrochemical properties of the film photodeposited without electrolyte are indistinguishable from those of experiment 1. A somewhat higher apparent coverage (3.6×10^{-8} mol/cm^2 of ferrocene sites) was attained.

Attempts to produce yet higher coverages by photodeposition were not successful as shown by results of experiments 4 and 5. Photolysis for 40 h (without n-Bu_4NClO_4) caused eventual fading of the green photolyzed solution's coloration and precipitation of a green solid which was presumed to be poly(vinylferrocenium) chloride but was not examined further. A higher coverage was not obtained for this extreme photolytic reaction [$\Gamma = 2.0 \times 10^{-8}$ mol/cm^2). A longer period of photolysis (7 days) under ambient illumination of a more concentrated (85 mM) poly(vinylferrocene) solution (experiment 5) gave $\Gamma = 2.6 \times 10^{-8}$ mol/cm^2 of ferrocene sites. These results indicate, in fact, that, under the photolysis conditions tested, a coverage of ca. 4×10^{-8} mol/cm^2 of ferrocene sites is a *limiting* coverage for the molecular weight of polyvinylferrocene used. There is no initially obvious reason why reaction 2 should involve a limiting coverage, given the prior electrochemical results[9a,18] and that the dissolved form of the polymer has become extensively photooxidized. For the 1 mL of 5 mM polymer solutions employed in experiments 1–4, photodeposition of the total quantity of polymer in this solution would produce a coverage of ca. 1×10^{-6} mol/cm^2, about 25× the observed limiting coverage.

An additionally puzzling result was obtained in the dark control for experiment 5, (experiment 6) which produced a coverage somewhat *larger* than the limiting coverage photolyzed result. Again, this film's electrochemical characteristics were similar to those of experiment 5.

The higher (26000) molecular weight poly(vinylferrocene) sample was photooxidized more rapidly, about 0.5 h being required to produce a degree of oxidation (by solution coloration) equivalent to that in experiment 1. In experiment 7, where photolysis of 26K polymer proceeded for 1 h, an apparent coverage of 2.4×10^{-8} mol/cm^2 of ferrocene sites was obtained, near the above-mentioned limit. In the same time period, in the dark (experiment 8), a coverage of 3.6×10^{-8} mol/cm^2 was obtained, again larger than the photolytic result. The cyclic voltammetry of these surfaces (Figure 2A,B) is qualitatively similar to that of the lower molecular weight sample (Figure 1A,B).

Understanding these results requires reconciliation of three facts: (i) initially, photolysis accelerates surface accumulation of poly(vinylferrocene), but (ii) the coverage reaches a limiting value, and (iii) the same or somewhat larger limiting coverage is attained without illumination, by spontaneous adsorption.

X-ray Photoelectron Spectroscopy. Insight into the above results comes from examination of the Fe $2p_{3/2}$ and Cl $2p_{3/2}$ XPS regions. Data from XPS experiments are given in Table I and pertinent spectra in Figure 3. Figure 3A shows the Fe $2p_{3/2}$ band observed on an electrode prepared by dark exposure to poly(vinylferrocene) solution (experiment 2). (This sample produced the cyclic voltammetry of Figure 1B). The well-

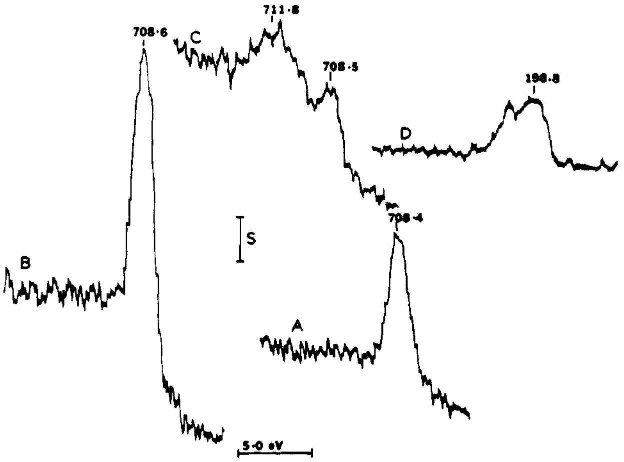


Figure 3. X-ray photoelectron spectroscopy of poly(vinylferrocene) films. Curve A: Fe $2p_{3/2}$ for film adsorbed in dark from CH_2Cl_2 solution (experiment 2, S = 256 counts/S). Curve B: Fe $2p_{3/2}$ for photodeposited film (experiment 1, S = 512 counts/S). Curve C: Fe $2p_{3/2}$ for film prepared by droplet evaporation of photolyzed solution from experiment 3 (S = 256 counts/S). Curve D: Cl 2p region for electrode of curve C (S = 256 counts/S).

defined band at 708.4 eV lies at precisely the binding energy expected for a reduced (ferrocene) species.[7]

A key observation is that a film deposited (experiment 1) from photolyzed solution also yields a spectrum (Figure 3B) indicative of *reduced* ferrocene. On the basis of reaction 2, plus unavoidable spontaneous adsorption, a mixture of ferrocene and ferrocenium oxidation states is expected in a film deposited under illumination. Ferrocenium is distinctive from ferrocene[7] in XPS, giving a broad band at 711–712 eV. The presence of a Cl $2p_{3/2}$ band would also be expected from the supporting electrolyte counterion of ferrocenium. However, neither ferrocenium Fe $2p_{3/2}$ (absent in Figure 3B), nor Cl $2p_{3/2}$ bands have been observed on any film deposited from photolyzed solution. Such films are in the reduced (ferrocene) state, contrary to expectations of reaction 2.

For demonstration of the detectability of ferrocenium in XPS of oxidized poly(vinylferrocene), samples of the green, photooxidized CH_2Cl_2 solutions in which the Pt electrodes had been immersed were evaporated on clean Pt disks and washed with methanol. Figure 3C,D shows the Fe $2p_{3/2}$ and Cl $2p_{3/2}$ regions, respectively, using the photooxidized solution of experiment 3. Both ferrocene (708.5 eV) and ferrocenium (711.8 eV) bands are clearly present, as is a Cl 2p band. This is typical for films prepared from an evaporated, photooxidized solution, confirming that photolysis of poly(vinylferrocene) solution in CH_2Cl_2 yields poly(vinylferrocenium), as expected (reaction 2). The poly(vinylferrocenium) state is also shown by these results not to undergo X-ray beam reduction during the spectral experiment nor is it washed off preferentially by the methanol rinsing procedure.

XPS spectra of fresh CH_2Cl_2 solutions of poly(vinylferrocene), prepared and evaporated on Pt in the dark, show only the 708.5-eV (reduced) ferrocene band and no Cl $2p_{3/2}$, as expected. The conditions of evaporation do not lead to oxidative production of poly(vinylferrocenium).

These results could be explained by either of the following: (i) the original hypothesis that photooxidation should be analogous to electrooxidation[9a] and lead to electrode coating by poly(vinylferrocenium) is wrong or (ii) poly(vinylferrocenium) is photodeposited but is reduced once a part of the surface film. The latter possibility is examined in the next section.

Reduction of Photodeposited Poly(vinylferrocenium)? Energetically, poly(vinylferrocenium), once deposited on Pt, could be reduced by photoelectric emission from the Pt, since the dominant line in the UV source employed exceeds the energy of the Pt work function (4.09 eV). Capture of photoemitted electrons by poly(vinylferrocenium) was ruled out by substituting SiO_2 for Pt as the substrate in a photolysis experiment (experiment 9), with no change in the essential result (only ferrocene, no ferrocenium, XPS band observed). The work function of SiO_2 is too large for a photoemission mechanism to be operative.

Poly(vinylferrocenium), once deposited on Pt, could alternatively become reduced if the $E°_{surf}'$ formal potential of the redox polymer film is more positive than the $E°_{soln}'$ of the dissolved polymer. This would lead to electron exchange between film and solution, reducing ferrocenium states in the film and generating further such states in the dissolved polymer. That such electron exchange can occur was demonstrated by the following experiments. Droplets of green, photooxidized poly(vinylferrocene) solution were evaporated to prepare several film samples, on which both ferrocene and ferrocenium XPS bands were evident (experiment 10), as discussed above. If such a film is exposed (dark) to a fresh solution of poly(vinylferrocene) in CH_2Cl_2, the film does not immediately redissolve and its XPS spectrum is unchanged; both 711.8-eV poly(vinylferricenium) and 708.5-eV poly(vinylferrocene) bands remain detectable. If the evaporatively prepared poly(vinylferrocene)–poly(vinylferrocenium) film is, on the other hand, *reexposed to the green, photooxidized solution from which it was prepared*, it does not immediately redissolve, and when it is examined by XPS, *only* a strong Fe $2p_{3/2}$ band for *reduced* ferrocene shows (708.8 eV, experiment 11). This result, coupled with the preceding controls, demonstrates[19a] that an *electron exchange occurs between poly(vinylferrocenium) sites in a deposited film and a reducing species present in a photolyzed CH_2Cl_2 solution of poly(vinylferrocene)*.

The electron-exchange process was further investigated by cyclic voltammetry in CH_2Cl_2 solution. Figure 1D shows a cyclic voltammogram in CH_2Cl_2 for a dark adsorbed film prepared as in experiment 2. The wave has an enhanced positive tail as compared to that in 0.1 M Et_4NClO_4/CH_3CN (see Figure 1B) but essentially the same formal potential, $E°_{surf}' = +0.38$ V vs. SSCE. (This film interestingly tolerated repeated potential cycling, although it dissolves eventually.)

Cyclic voltammetry of 1 mM polyvinylferrocene dissolved in CH_2Cl_2 is shown in Figure 2C,D. Since Merz and Bard[9a] showed that cycling a Pt electrode in poly(vinylferrocene) solutions in CH_2Cl_2 results in deposition of films of redox polymer, data in Figure 2C–D corresponds to the virgin or second potential scan on freshly cleaned (polished) Pt surfaces, to maximize the response of the dissolved form of the polymer. At 100-mV/s potential scan rate, the broadened voltammogram (Figure 2C) has ΔE_{peak} = 230 mV and ($E°_{soln}'$) formal potential (average of anodic and cathodic waves) of 0.41 V vs. SSCE, which is 30 mV more positive than $E°_{surf}'$ of the polymer film in CH_2Cl_2 (Figure 1D). A difference between $E°_{soln}'$ and $E°_{surf}'$ of this magnitude is common.[19b] At slow scan rate (Figure 2D), the peaks sharpen and the anodic wave resolves into two components. The charge under the first member of the anodic wave amounts to 1–3 monolayer equivalents of ferrocene sites, so this wave may be an adsorption prewave. A solution of 26K polymer in CH_2Cl_2 gives a voltammetric response like Figure 2D even at 100 mV/s, with $E°_{soln}'$ varying from 0.36 to 0.41 V vs. SSCE.

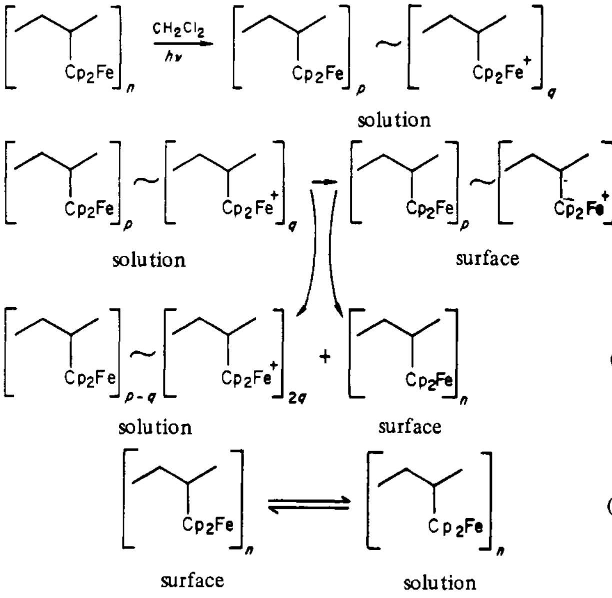
---

(19) (a) A reviewer has raised the possibility of the photodeposited polyvinylferrocene films being reduced because they are caused by polymerizing effects of solvent photoproduct radicals. This electron-exchange experiment weighs against this hypothesis. (b) Lenhard, J. R.; Rocklin, R.; Abruña, H.; Willman, K.; Kuo, K.; Nowak, R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 521.

Again with clean Pt, Figure 2E,F show cyclic voltammetry of the solution used for Figure 2C,D after photolysis for 1.7 h (experiment 9). Results in this green solution are very similar to those in the original solution, except—a key point—the waves are shifted to more negative potentials by ca. 100 mV so that $E^{\circ}_{\text{soln}}{}'$ (now +0.30 V) of the photolyzed solution is now ca. 80 mV negative of that $E^{\circ}_{\text{surf}}{}'$ (+0.38 V) of the photodeposited film. The difference in potential shows that the *photolyzed solution ferrocene sites are more reducing than those of the photodeposited film* and is sufficiently large as to cause reduction of greater than 90% of the ferrocenium sites in a redox polymer film contacting this solution.

The chemical basis for the cathodic shift in $E^{\circ}_{\text{soln}}{}'$ of poly(vinylferrocene) upon photolysis is not entirely clear. Some chemical changes in the dissolved polymer may occur via attack by $CH_2Cl\cdot$ radicals (reaction 2). On occasion, a minor diffusional wave appears at −0.04 V vs. SSCE in a photolyzed CH_2Cl_2 solution of poly(vinylferrocene) which might be a decay product. This wave is not observed prior to photolysis or in any of the polymer films, however deposited. A second possibility is ion pairing or other coordinative effects of chloride generated in reaction 2. Indeed, addition of $(CH_3)_4NCl$ to a solution of poly(vinylferrocene) in CH_2Cl_2 caused, without photolysis, a 30-mV negative shift of $E^{\circ}_{\text{soln}}{}'$, and a trace of the −0.04-V wave appeared after about 30 min. Chloride thus produces a formal potential shift in the required direction, but concurrent effects of other chemistry may also play a role.

The scheme shown in eq 3–5 is proposed to represent the above results. Reaction 3 is expected to occur by analogy with the electrooxidation result of Merz and Bard,[9a] that poly(vinylferrocenium) will accumulate on Pt from CH_2Cl_2 solution. Reaction 5 corresponds to the dark adsorption process described here. To the extent that reaction 3 occurs, however, ferrocenium sites in the deposited film become reduced (because of the difference in $E^{\circ\prime}$ values) by ferrocene sites in the dissolved polymer (reaction 4). In this way, the oxidized form of the polymer is forced to accumulate in the solution, until a sufficient fraction of the ferrocene sites become oxidized so that the polymer chains physically aggregate and precipitate as a green solid. The coverage of polymer which accumulates on the Pt is also constrained by reaction 4 to be no more than that allowed by reaction 5; e.g., no matter how extensive the photolysis reaction, adsorption via reaction 3 becomes in effect cancelled by the ensuing electron exchange of reaction 4. Unphotolyzed solutions contain a higher concentration of (reduced) poly(vinylferrocene) than do photooxidized solutions, so the limiting coverage of redox polymer in the photolytic experiments is less than that produced by dark adsorption for the same period of exposure.



(3)

(4)

(5)

Characterization of Photodeposited Polymer by Weight. In order to estimate the fraction of deposited redox polymer which is electrochemically reactive, we exposed a larger (6.25 cm^2) weighed Pt foil to an irradiated (15 h) poly(vinylferrocene) solution in CH_2Cl_2 and then reweighed after thorough washing with methanol and vacuum-oven drying. A deposited mass of 236 μg was thereby measured. The charge under the voltammetric wave for this electrode corresponded to 6.2×10^{-7} mol of ferrocene sites, amounting to an apparent equivalent weight of 380. Given the mass of 212 of monomer vinylferrocene, this result shows that the photodeposited film exhibits ca. 56% of its ideally expected electrochemistry. This percentage is probably low since complete removal of solvent is difficult, but the difference from ideality is great enough to suggest that deposited polymer contains some demetallated radical damage sites or that some ferrocene sites are in poor electron-transfer contact with the electrode.

Angular Resolved X-ray Photoelectron Spectroscopy. There are few available methods for thickness determination for very thin organic films. One is XPS, measuring photoelectron emission intensity of the substrate as a function of angle θ relative to the coated surface.[20] In experiments detailed elsewhere[21] we have applied variable angle XPS to six transition-metal polymer films, including those prepared in experiments 7 and 8. According to the 1.25 g/cm^3 density of the 26K poly(vinylferrocene) these two films should have an average dry thickness of 411 (experiment 7) and 616 Å (experiment 8), which in comparison to the estimated[21,22] 23.5 Å escape depth for Pt 4f photoelectrons through poly(vinylferrocene) should allow only a miniscule Pt 4f photoelectron emission even at normal (θ = 90°) angle. Significant Pt 4f peaks were nonetheless observable on these samples and gave apparent but erroneous XPS film thicknesses of 58 and 41 Å, respectively.[21]

These results suggest that the dark adsorbed and photodeposited films have substantial topological nonuniformity, in which naked or very thinly covered Pt is exposed. The XPS experiment is quite sensitive to film thickness nonuniformity;[20] for the film is experiment 7 only ca. 8% of the Pt electrode need be naked to yield Pt 4f photoelectrons of the observed intensity.

The other four polymer films studied[21] by variable-angle XPS gave film thickness differing from electrochemically derived ones by factors ranging from 20% to 250%, but in the opposite direction, indicating that those redox polymer films were free from substantial thickness nonuniformities.

Photolytic Initiation of Vinylferrocene Polymerization. Polymerization of vinylferrocene can be initiated by free radicals,[18] and it was of interest whether a film of redox polymer could be generated by simultaneous photopolymerization and photodeposition. A 47 mM solution of vinylferrocene in CH_2Cl_2 solvent was irradiated for 15 h (Table I, experiment 12) in contact with a Pt surface. A ferrocene wave was observed subsequently, as was Fe $2p_{3/2}$ XPS. The coverage was rather low but was higher than can be accounted for by vinylferrocene chemisorption on Pt, so photopolymerization apparently did occur.

Electrochemical Characteristics of Poly(vinylferrocene) Films. Poly(vinylverrocene) films have been deposited on electrodes by electrochemical precipitation[9] and by radiofrequency plasma polymerization of vinylferrocene.[7,8,10] It was

---

(20) Fadley, C. S. *J. Electron. Spectrosc. Relat. Phenom.* **1974**, *5*, 725.
(21) Umaña, M.; Denisevich, P.; Rolison, D. R.; Nakahama, S.; Murray, R. W. *Anal. Chem.* **1981**, *53*, 1170.
(22) Penn, D. R. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *9*, 29.

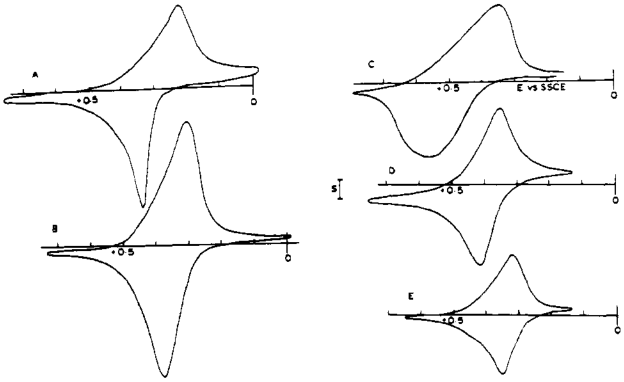


Figure 4. Cyclic voltammetry of films of poly(vinylferrocene) prepared by dark adsorption from CH_2Cl_2 solution (experiment 6). Curve A: in 0.5 M $LiClO_4$/water, 50 mV/s, $S = 52\ \mu A/cm^2$. Curve B: in 1 M Et_4NClO_4/CH_3CN, 50 mV/s, $S = 298\ \mu A/cm^2$. Curve C: in 0.01 M Et_4NClO_4/CH_3CN, 5 mV/s, $S = 21\ \mu A/cm^2$, $\Delta E_p = 262$ mV. Curve D: in 0.1 M Et_4NClO_4/CH_3CN, 5 mV/s, $S = 20\ \mu A/cm^2$, $\Delta E_p = 60$ mV, $E_{fwhm} = 119$ (anodic) and 117 mV (cathodic). Curve E: in 1 M Et_4NClO_4/CH_3CN, 5 mV/s, $S = 44\ \mu A/cm^2$, $\Delta E_p = 28$ mV, $E_{fwhm} = 90$ (anodic) and 120 mV (cathodic).

of interest to compare electrochemical properties of poly(vinylferrocene) films among the deposition procedures used here, photochemical deposition, dark spontaneous adsorption, and droplet evaporation, and earlier. Variation of electrochemical characteristics with deposition method is potentially important as applications of redox polymer films proliferate.

Peerce and Bard[23] observed an additonal wave (their class 3) lying ca. 100 mV positive of the main ferrocene wave in films of electrochemically precipitated poly(vinylferrocene), especially at slow potential sweep rates where the main was ΔE_p decreased and E_{fwhm} narrowed. Both anodic and cathodic branches of the ferrocene waves in Figure 1 and 4B,E exhibit a slight symmetrical swelling on the positive potential side, indicative of the presence of a more positive ferrocene state (albeit in minor proportions) in our results as well. The extra wave is, qualitatively, more apparent at high supporting electrolyte concentration (compare Figure 4C–E), in Et_4NClO_4 electrolyte vs. Bu_4NClO_4 (compare Figure 1A,C), and in CH_2Cl_2 as compared to CH_3CN solvent (compare Figure 1B,D). The additional ferrocene state in films of poly(vinylferrocene) is thus not peculiar to a given deposition mode and is sensitive to the environment of the polymer film, as might be expected if solvent swelling factors[10c] are in part responsible for this electrochemical nonequivalence of ferrocene states.

The photochemically and dark adsorbed poly(vinylferrocene) films exhibit qualitatively but not quantitatively the wave shapes observed in water solvent for plasma polymerized vinylferrocene films[8,10c] and for aminophenylferrocene coupled to a siloxane polymer,[10e] i.e., an anodic wave sharpened relative to the cathodic member (Figure 4A). However, even at very low potential sweep rates, the anodic wave in the present films does not undergo the extreme narrowing seen for the other films. The anodic wave narrowing is an activity phenomenon,[8] in which a phaselike ferrocene site activity behavior results presumably from low solvent swelling in water, and this effect seems accentuated by the cross-linked circumstances of the plasma polymerized and siloxane films.

Activity (wave narrowing, E_{fwhm}) effects in CH_3CN for photochemically deposited polyvinylferrocene films are slightly different from those of films prepared by evaporating droplets of the same, photolyzed solution; see Figure 1C,E and E_{fwhm} data in Table II. The smaller E_{fwhm} for the evaporated films means that the ferrocene/ferrocenium activity ratio varies less over the course of exhaustive film oxidation than is the case for the photolytically deposited films. The narrowing of the surface-state energy this represents is a potentially important distinction in rectifying applications.[6,24] The evaporated films also tend to be less resistive (smaller ΔE_p), but there is no discernible difference in formal potential (Table II).

Table II. Comparison of Cyclic Voltammetry of Photochemically Deposited Poly(vinylferrocene) Films (Experiment 1) and Films Prepared by Evaporation of Droplets of Photolyzed Solution, in 0.1 M Et_4NClO_4/CH_3CN

wave, mV/s	$E^\circ{}_{surf}{}'$ vs. SSCE photo	evap	ΔE_p, mV photo	evap	E_{fwhm} (photo/evap), mV anodic	cathodic
20	0.39	0.39	38	15	127/68	122/95
50	0.39	0.39	52	20	132/82	124/98
100	0.39	0.39	72	24	160/88	145/102
200	0.40	0.39	95	26	173/102	167/108

Table III. Stability of Ferrocene Polymer Films in Terms of Half-Life of Ferrocenium State

sample photodeposited	supporting electrolyte[a]	$10^8\Gamma_{t=0}$, mol/cm²	$t_{1/2}$, min[b]
expt 5	1 M Et_4NClO_4	2.8	127
expt 1	0.1 M Et_4NClO_4	2.3	75
plasma polymer[c]	supporting electrolyte[a]	$10^9\Gamma_{t=0}$, mol/cm²	$t_{1/2}$, min[b]
1 day	0.1 M Et_4NClO_4	2.2	8
8 days	0.1 M Et_4NClO_4	2.3	13
30 days	0.1 M Et_4NClO_4	5.8	23
15 days	1 M $LiClO_4$	5.2	71
25 days	0.1 M $LiClO_4$	7.3	135

[a] Solvent is CH_3CN dried over molecular sieves. [b] Time required for the charge under the cyclic voltammetric ferrocene ⇌ ferrocenium wave (0.2 V/s) to decrease to half the original value ($\Gamma_{t=0}$) as a result of potentiostating at +0.75 V vs. SSCE, with periodic cyclic voltammograms taken. [c] From a set of samples prepared in one batch, by a procedure described elsewhere,[10d] and aged (dry, in air) for stated period.

Finally, Figure 4C–E shows the effect of supporting-electrolyte concentration. Wave broadness and ΔE_p increase as $[Et_4NClO_4]$ is lowered, but the quantitiy of charge under the wave does not change. The voltammetric peak current calculated for 10 mM ClO_4^- diffusing in CH_3CN is ca. 10× larger than the peak current observed in Figure 4C, which means that the wave-shape change cannot be attributed to concentration polarization of the electrolyte counterion in the contacting solution.[10c] The effects seen are plausibly attributed to low internal electrolyte concentration in the film with consequent uncompensated resistance effect. Other potential step studies, of plasma polymer films, have shown that[8] lowering of electrolyte concentration from 1.0 to 0.5 M has an appreciable film resistance penalty but that the rate of charge transport across the film remains constant if extra potential increments are added to compensate for the film resistance.

Stability of Redox Polymer Films. The lifetime of ferrocene ⇌ ferrocenium electroactivity in poly(vinylferrocene) films prepared here and in plasma polymerized vinylferrocene films[8,10] is determined by a decay process occurring when the film is in the ferrocenium state. The reduced films survive days of exposure to acetonitrile solvent, but when potentiostated at +0.75 V vs. SSCE, in the poly(vinylferrocenium) state, with periodic cyclic potential sweeping to assay the remaining charge under the cyclic voltammetric peak, the film decays

---

[23] Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89.

[24] Denisevich, P.; Abruña, H. D.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1.

at a perceptible rate. During the decay, the periodically taken cyclic voltammetric peaks gradually become shaped more like diffusional waves, and uncertainties in the coverage assay associated with this shape change make an adequately convincing inspection of the decay rate law difficult. Some useful insights can be gained simply from the time required for the apparent coverage of electroactive sites in the film to decrease to half the initial value. Such $t_{1/2}$ data are given in Table IIII.

The life data confirm[10d] that aging considerably increases the stability of plasma polymerized vinylferrocene films and also suggest that film stability varies with electrolyte. The data further show that only after weeks of aging do the plasma polymer films achieve the same stability as the preformed, photodeposited polymer, which has a half-life of 1-2 h. The aging effect may thus be less associated with a kinetics change for the chemistry by which ferrocenium sites are degraded than with a slow binding of low molecular weight oligomers in the plasma polymer to its cross-linked framework, avoiding loss of these units via leaching from the ferrocenium state film.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation. This is publication 28 in a series on Chemically Modified Electrodes.

Registry No. Poly(vinylferrocene), 34801-99-5; Pt, 7440-06-4.

Contribution from the Max-Planck-Institut für Strahlenchemie,
D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

Photochemical Cleavage and Recombination Reactions of Matrix-Isolated (1-σ-4–6-η^3-Organo)tricarbonyliron Complexes

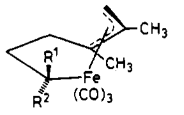
FRIEDRICH-WILHELM GREVELS* and WERNER E. KLOTZBÜCHER*

Received August 12, 1980

UV–visible irradiation of two isomeric (1-σ-4–6-η^3-organo)Fe(CO)$_3$ complexes, adducts of methyl acrylate and (η^4-dimethylbutadiene)tricarbonyliron, in inert and reactive matrices at 10–12 K was monitored by IR and UV spectroscopy. Detachment of CO is the only primary photoreaction. Subsequent reactions depend on the orientation of the ester group in the two isomers. Either the ester group is photoreversibly coordinated or the ejected CO is recaptured. Effective, stereospecific incorporation of a ligand from the matrix environment is observed for one of the isomers in experiments with ^{13}CO and N$_2$ matrices.

Introduction

Extended irradiation of pentacarbonyliron in the presence of olefin/1,3-diene mixtures results in coupling of the unsaturated substrates with formation of (1-σ-4–6-η^3-organo)tricarbonyliron complexes.[1,2] In particular, the substrate combination methyl acrylate/2,3-dimethylbutadiene yields two isomeric products, **1a** and **1b**,[1] which both are formed via either the (η^4-diene)Fe(CO)$_3$ or (η^2-olefin)Fe(CO)$_4$ complexes. More recently, (η^4-dimethylbutadiene)(η^2-methyl acrylate)dicarbonyliron (**2**) has been isolated as the key intermediate which reacts in the dark with carbon monoxide to form **1a** and **1b**.[3] Furthermore, **1a** and **1b** were shown[4] to undergo photochemical interconversion, **1a** $\rightleftarrows$ **1b**; concomitantly photocleavage leads back to (η^4-diene)Fe(CO)$_3$ and methyl acrylate, thus reducing the overall yield of **1**.



1a: R^1 = H, R^2 = CO$_2$CH$_3$
1b: R^1 = CO$_2$CH$_3$, R^2 = H

In order to obtain information about the intermediates involved in these reactions, we are investigating the photochemical behavior of the source materials and the products under low-temperature matrix-isolation conditions. A study with (η^4-diene)Fe(CO)$_3$ complexes has been reported previously.[5] In the present work we examine the photochemistry of the adducts **1a** and **1b** in inert and reactive matrices.

Experimental Section

Several details of the experimental equipment used in our photochemical and spectroscopic low-temperature investigations have been described previously.[5] An Air Products Displex closed-cycle helium cryostat was employed to cool a NaCl optical window to 10–12 K, the temperature being monitored by a thermocouple embedded in a drilled cavity close to the window center. The flow of matrix gas (99.99%, L'Air Liquide) was controlled by a calibrated micrometer needle valve and vacuum meter assembly, adjusted for each gas to a flow of approximately 2 mmol/h by a He–Ne laser interference fringe test.[6] The samples, purified and transferred under argon atmosphere, were deposited from a glass capillary held at constant temperature (32 °C for **1a**, 17 °C for **1b**) by a Peltier element, the temperature of which was separately monitored. In general a dilution of 1:1000 was attempted.

Infrared spectra were recorded on a Perkin-Elmer 580 instrument with the visible radiation (from the Nernst glower) removed by an Oriel CdTe filter. UV-visible spectra were taken with a Perkin-Elmer 356 two-wavelength spectrometer operating in the Split mode. For photochemical experiments the output of a Philips HPK 125 W high pressure mercury lamp was filtered through a 5-cm water cell to obtain "white" light with most of the infrared radiation removed. An air-cooled Schott GG 495 cutoff filter ($\lambda \gtrsim 495$ nm) replaced the cell for long-wavelength irradiations.

Results

The samples and their products were characterized by the CO stretching vibration patterns of the Fe(CO)$_n$ moieties and the CO stretching mode of the ester group in the infrared spectra and by the electronic absorptions in the UV–visible spectra. As the matrix-isolated compounds **1a** and **1b** behave somewhat differently in the irradiation experiments, they will be treated separately.

1. Irradiations of 1a. (a) In Inert-Gas Matrices. Figure 1A displays the characteristic Fe(CO)$_3$ pattern of **1a** isolated in argon at 10–12 K. The three strong absorptions appear in argon at 2068, 2012, and 1990 cm^{-1} and shift only slightly in different matrix materials (cf. Table I). In the ester carbonyl

---

(1) F.-W. Grevels, U. Feldhoff, J. Leitich, and C. Krüger, *J. Organomet. Chem.*, **118**, 79 (1976).
(2) F.-W. Grevels and I. Salama, to be submitted for publication.
(3) F.-W. Grevels and K. Schneider, *Angew. Chem.*, **93**, 417 (1981); *Angew. Chem., Int. Ed. Engl.*, **20**, 410 (1981).
(4) T. Akiyama and F.-W. Grevels, to be submitted for publication.
(5) G. Ellerhorst, W. Gerhartz, and F.-W. Grevels, *Inorg. Chem.*, **19**, 67 (1980).
(6) P. Groner, I. Stolkin, and Hs.H. Günthard, *J. Phys. E*, **6**, 122 (1973).

0020-1669/81/1320-3002$01.25/0