An Electrochemical Investigation of Photosubstitution Processes at Glassy-Carbon Electrodes Coated with Polymer-Bound Ruthenium Complexes

Otto Haas,* Monika Kriens, and Johannes G. Vos

Contribution from the Institute of Inorganic Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland. Received July 7, 1980

Abstract: Glassy-carbon electrodes were coated with [Ru(bpy)$_2$Cl(poly(4-vinylpyridine))]Cl. These derivatized electrodes were photolyzed while cyclic voltammograms were recorded. The changes of redox potential observed in the cyclic voltammograms are explained in terms of ligand exchange of the coordinated Cl$^-$ with H$_2$O, ClO$_4^-$, and CH$_3$CN. This opens an easy way to change the redox potential of a fixed ruthenium complex. The demonstrated exchange processes are irreversible. Therefore an information storage, which can be read with suitable electrochemical equipment, is possible.

Surface-attached redox systems have been widely used in catalytic and electrochemical domains.[1] The catalytic effect of such systems may easily be investigated by using suitable electrodes as probes. The so-called derivatized electrode is the product of such studies. A number of interesting papers dealing with ruthenium complexes attached to poly(4-vinylpyridine) (PVP) have been published recently.[2] These redox systems are of particular interest when they are attached to a surface, as they may be used to protect photoanodes from photocorrosion,[3] and they can act as sensitizers in solar energy devices.[4] It seems, therefore, worthwhile to study the photochemistry of such polymers attached to electrodes.

In an earlier report,[5] we described the preparation and the electrochemistry of [Ru(bpy)$_2$Cl(PVP)]Cl coated electrodes (bpy = 2,2'-bipyridyl). In this paper, we wish to report some photosubstitution reactions of these polymer-bound ruthenium complexes which are attached to glassy-carbon electrodes. As far as we know, this is the first time that photosubstitution reactions of surface attached systems are reported.

An interesting aspect of the photosubstitution is the fact that the redox potential of the fixed ruthenium complex is changed markedly. This is particularly important in cases where the coating is to be used to protect the photoanodes or to catalyze a redox couple. The redox potential of the coating must then be matched to the redox couple in question. This adjustment is now easily achieved by first carrying out a directed photosubstitution. Although in principal the photosubstitution could be done in homogeneous solution, the reaction at the electrode surface is carried out more easily. Another interesting aspect is the irreversibility of the photosubstitution. This offers the possibility of information storage.

So that the photosubstitution process could be studied, [Ru(bpy)$_2$Cl(PVP)]Cl coated glassy-carbon electrodes[6] were irradiated with visible light (500-W projector lamp), and the reactions were followed by recording the cyclic voltammograms obtained during

the photolysis. A 1.0 M aqueous solution of HClO$_4$ and a 0.5 M solution of LiClO$_4$ in acetonitrile were used as supporting electrolytes. Figure 1 shows the CV waves recorded during the photolysis of an electrode in 1.0 M HClO$_4$. The wave at 640 mV vs. SCE disappears, and a new signal at 840 mV is produced. We attribute this change in potential to a photosubstitution process in which the Cl$^-$ ligand is exchanged photochemically for some other ligand, L, depending on the electrolyte.[8]

$$[Ru(bpy)_2Cl(PVP)]^+ \xrightarrow[\text{electrolyte}]{h\nu + L} [Ru(bpy)_2L(PVP)]^{n+}$$

$$L = H_2O, ClO_4^-, CH_3CN; \ n = 1,2$$
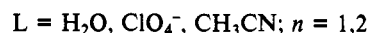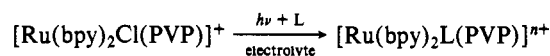
The photosubstitution can be rationalized as follows. Under irradiation a MLCT to an antibonding π^* orbital takes place and, via intersystem crossing, a triplet state ^{3}CT becomes occupied. Since this ^{3}CT state is in thermal equilibrium with antibonding σ^* LF states, the Ru–ligand bond is weakened and the photosubstitution is facilitated.[10]

The changes observed in the UV/vis spectra of the photolyzed polymers are consistent with such a reaction. UV/vis spectra were obtained from coated UV cells in the presence of an electrolyte. The cells were coated in the same way as the electrodes to get comparable conditions.

We believe that, in aqueous HClO$_4$, the photoproduct obtained is [Ru(bpy)$_2$(H$_2$O)(PVP)]$^{2+}$. The position of the redox potential (840 mV vs. SCE), its behavior toward a change of pH, and the UV/vis spectrum (λ_{max} = 472 nm in H$_2$O (1.0 M HClO$_4$)) strongly point in this direction.[5,9,11] If a [Ru(bpy)$_2$Cl(PVP)]Cl coated electrode is irradiated in a 0.5 M solution of LiClO$_4$ in acetonitrile, two waves at 945 and 1135 mV vs. SCE are developed while the starting signal at 640 mV is disappearing. If the light is switched off, the wave at 945 mV disappears and the 1135-mV signal becomes stronger. The wave at 945 mV reappears, if the electrode is illuminated again. The signal at 1135 mV probably corresponds to the [Ru(bpy)$_2$(CH$_3$CN)(PVP)]$^{2+}$ complex.[12] Having only ClO$_4^-$ and CH$_3$CN in the solution, we assume that the wave at 945 mV is due to the perchlorato complex, but the presence of the aquo complex can not be ruled out, as the electrolyte solution may contain some water. The [Ru(bpy)$_2$(ClO$_4$)(py)]$^+$ complex (py = pyridine) can indeed be isolated from an irradiated [Ru(bpy)$_2$(py)$_2$]$^{2+}$ solution in CH$_2$Cl$_2$; in aqueous solution, however, this complex does not seem to be stable. Figure 2 shows that the acetonitrile complex is thermodynamically more

(1) Snell K. D.; Keenan, A. G. *Chem. Soc. Rev.* **1979** 8, 259.

(2) (a) Oyama N.; Anson, F. C. *J. Am. Chem. Soc.* **1979**, *101*, 3450. (b) *Ibid.* 739. (c) Abruña, H. D.; Walsh, J. L.; Meyer T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3272.

(3) (a) Haas, O.; Müller, N.; Gerischer, H., to be submitted for publication. (b) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis N. S.; Wrighton, M. S., *J. Am. Chem. Soc.* **1979**, *101*, 1378.

(4) (a) Gerischer, H. *Photochem. Photobiol.* **1972**, *16*, 243. (b) Mackor A.; Schoonman, J. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 71.

(5) Haas O.; Vos, J. G. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *113*, 139.

(6) [Ru(bpy)$_2$Cl(PVP)]Cl was prepared as described.[7] The electrodes were prepared by putting a drop of a 1% solution of the polymer in methanol on the electrode surface and evaporating the solvent.[5] The surface coverage with Ru complex is about 5 × 10^{-9} M/cm^2. The analysis of the [Ru(bpy)$_2$Cl(PVP)]Cl complex shows that about every fifth pyridine is coordinated to a Ru center. From the preparation method used we assume a molecular weight of about 100 000 for the PVP polymer.

(7) Clear, J. M.; Kelly, J. M.; Pepper D. C.; Vos, J. G. *Inorg. Chim. Acta* **1979**, *33*, L 139.

(8) Similar photosubstitution reactions have been observed for this polymer in solution and also for related ruthenium compounds.[7,9]

(9) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860.

(10) van Houten J.; Watts, W. J. *Inorg. Chem.* **1978**, *17*, 3381.

(11) Meyer, T. J.; personal communication.

(12) Meyer[9] found a value of 1.35 V vs. SCE in acetonitrile for the complex [Ru(bpy)$_2$(CH$_3$CN)(py)]$^{2+}$. Our potential was measured with an aqueous SCE electrode without correction for junction potential.[15]
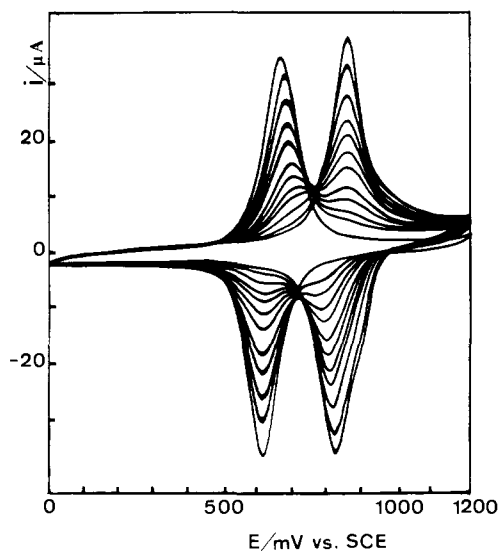
Figure 1. Cyclic voltammograms recorded during the photolysis of a [Ru(bpy)$_2$Cl(PVP)]Cl coated glassy-carbon electrode using a 1.0 M aqueous solution of HClO$_4$ as an electrolyte. The wave at 640 mV vs. SCE decreases whereas the wave at 840 mV increases. Diameter of the electrode 3 mm; scan rate 100 mV/s. The time elapsed between cycles is continuously increased from 0.5 to 2 minutes.
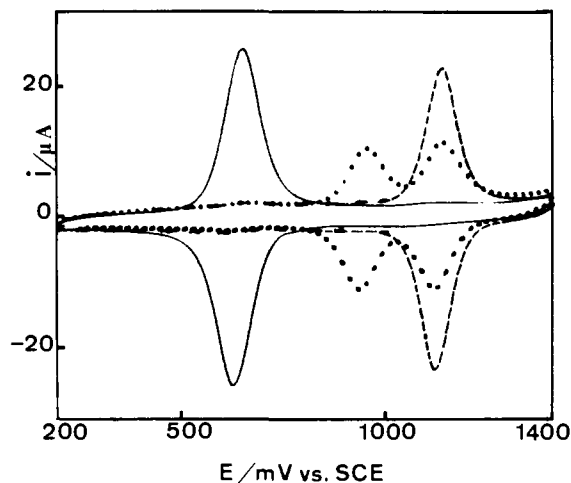

Figure 2. Cyclic voltammograms of a [Ru(bpy)$_2$Cl(PVP)]Cl coated glassy-carbon electrode with a 0.5 M solution of LiClO$_4$ in acetonitrile as an electrolyte: (—) before irradiation; (⋯) during irradiation (stationary state after 5 min); (- - -) after switching of the light and equilibrating for 5 min.

stable than the perchlorato complex. Under irradiation, however, the equilibrium is displaced toward the perchlorato complex.

From these observations, it is clear that the nature of the photo product depends strongly on the electrolyte. This provides us with the possibility of synthesizing a whole range of new coatings, starting from the basic and easily obtained [Ru(bpy)$_2$Cl(PVP)]Cl polymer. The photosubstitutions normally take just a few minutes. The process is faster if the electrode is held at a negative potential when irradiated. If the electrode is held at a potential more positive than the potential of [Ru(bpy)$_2$Cl(PVP)]Cl, no photosubstitution is observed and the signal just decreases very slowly.[13] Some of the photosubstitutions are certainly only photocatalyzed reactions, and, therefore, they are irreversible. This offers the possibility of information storage. The coated electrode obviously remembers
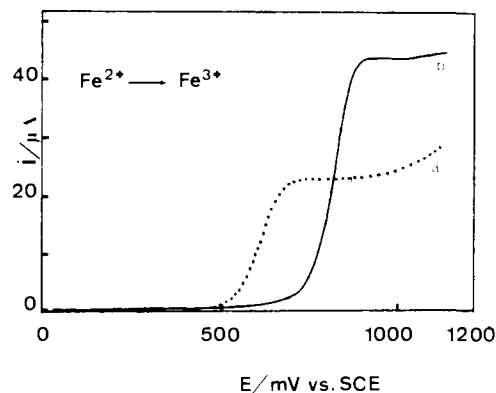
Figure 3. Current voltage curves of a 10^{-2} M aqueous solution of (NH$_4$)$_2$Fe(SO$_4$)$_2$ with use of a [Ru(bpy)$_2$Cl(PVP)]Cl coated rotating electrode: (a) before photosubstitution; (b) after photosubstitution. Experimental conditions: electrolyte 1 M HClO$_4$; rotation speed 16.6 Hz; scan rate 2 mV/s; diameter of the electrode 2 mm.

whether it was irradiated or not, and this information can be read with electrochemical equipment. Figure 3 shows that it is possible to translate this information to another redox system. We demonstrated before[5] that the rate of the oxidation of Fe(II) is markedly increased if a [Ru(bpy)$_2$Cl(PVP)]Cl coated glassy-carbon electrode is used instead of an untreated one. The polymer coating inhibits the oxidation until the Ru(II) centers are oxidized. This mediated electron-transfer[5] process is also observed at the [Ru(bpy)$_2$(H$_2$O)(PVP)]$^{2+}$ coated electrode (see Figure 3). The wave appears at a more positive potential corresponding to the redox potential of the aquo complex. This means that in 1.0 M HClO$_4$ the rotating [Ru(bpy)$_2$Cl(PVP)]Cl coated electrode oxidizes Fe(II) at 640 mV whereas the same electrode, after irradiation, oxidizes Fe(II) at a more positive potential. A yes/no device is obtained if the electrode is held at an intermediate potential of, say, 740 mV. The irradiated electrode shows no current while with the unirradiated one an anodic current is observed. The fact that the two electrodes show different limited currents needs some explanation. Under the experimental conditions, the diffusion-limited current (85 μA) is not reached in both cases. We showed in an earlier paper[5] that for such modified electrodes the current depends on the rate constant, k, of the reaction between the coating and the redox couple in solution

$$[Ru^{III}(bpy)_2Cl(PVP)]^{2+} + Fe(II) \xrightarrow{k_1}$$
$$[Ru^{II}(bpy)_2Cl(PVP)]^+ + Fe(III)$$

$$[Ru^{III}(bpy)_2(H_2O)(PVP)]^{3+} + Fe(II) \xrightarrow{k_2}$$
$$[Ru^{II}(bpy)_2(H_2O)(PVP)]^{2+} + Fe(III)$$

For other redox systems attached to electrodes, similar behavior has been observed.[14]

ΔG for the second reaction is more negative, so k_2 should be greater than k_1. Since the amount of fixed ruthenium remains constant during the photosubstitution process, a bigger anodic current for the [Ru(bpy)$_2$(H$_2$O)(PVP)]$^{2+}$ coating is expected.

Investigators using other potential ligands are in progress.

(13) Since the Ru–Cl bond in Ru^{III}–chloro complexes is very strong, it seems likely that the Ru–PVP bond is broken instead of the Ru–Cl bond when the polymer is irradiated at high positive potentials.
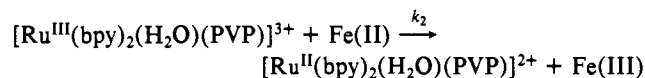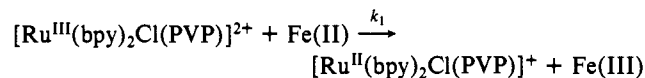
(14) Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192. Albery, W. J.; Foulds, A. W.; Hall K. J.; Hillman, A. R. *J. Electrochem. Soc.* **1980**, *127*, 654.

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