ELSEVIER

Journal of Organometallic Chemistry 637–639 (2001) 841–844

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Note

Anion effect on the electrochemical characteristics of a gold electrode modified with a self-assembled monolayer of ferrocenylhexanethiol in aqueous and dichloromethane solutions

Toshihiro Kondo *, Masayuki Okamura, Kohei Uosaki

Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received 20 April 2001; received in revised form 2 May 2001; accepted 2 May 2001

Abstract

The electrochemical characteristics of a gold electrode modified with a self-assembled monolayer (SAM) of ferrocenylhexanethiol were investigated in aqueous and dichloromethane solutions containing various anions, i.e. HSO_4^- (or SO_4^{2-}), ClO_4^-, and PF_6^-. In all the cases, a pair of redox peaks corresponding to the redox of a ferrocene moiety in a SAM was observed. The peak positions depended on the anions in the solution. While the redox potential measured in the aqueous solutions shifted more positively in the anion order of PF_6^-, ClO_4^-, and HSO_4^-, that measured in dichloromethane shifted more negatively in this order. The origin of this anion effect on the redox potentials in the aqueous and dichloromethane solutions was discussed by comparing the electrochemical characteristics of the results for ferrocene dissolved in dichloromethane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Self-assembled monolayer; Ferrocene; Alkanethiol SAM on gold; Anion effect; Organic solvent

---

1. Introduction

Ferrocene possesses many interesting properties and attracts research workers in many fields including electrochemistry. It is known that the redox reaction of ferrocene (Fc)/ferricenium cation (Fc^+) is completely reversible and the redox potential of Fc/Fc^+ is not significantly dependent on the solvent [1]. Thus, ferrocene is recommended by the IUPAC to be used as an internal reference for electrochemical measurements in various media [2] and has been used in various fields, including the chemically modified electrodes where ferrocene is one of the most popular electrochemically active groups [1].

The self-assembly (SA) technique has been very widely used to construct molecular ordered layers with various functionalities, and the self-assembled monolayers (SAMs) of alkanethiols on gold have been the most well studied system in the last decade [3,4]. At the beginning of the 1990s, Chidsey et al. [5] and our group [6,7] reported the electrochemical properties of gold electrodes modified with the SAMs of ferrocene-terminated alkanethiols in aqueous solutions. After these reports, many groups constructed similar systems containing the ferrocene group and studied their electrochemical properties [8–11]. Although it is interesting and important to investigate the electrochemical characteristics of the SAM modified electrodes in organic solvents both for fundamental science and for industrial applications such as sensors and electronic molecular devices, most of the studies on the electrodes modified with SAM containing not only ferrocene but also other electrochemically active groups were carried out in the aqueous solutions. To extend the chemically modified electrode to organic solvents, it is important to investigate the effects of the solvents and ions on its electrochemical characteristics.

In this study, we employed ferrocene as an electrochemically active group fixed into the SAM and mea-

---

* Corresponding author. Fax: +81-11-746-2557.

E-mail address: kondo@pchem.sci.hokudai.ac.jp (T. Kondo).

PII: S0022-328X(01)00985-8

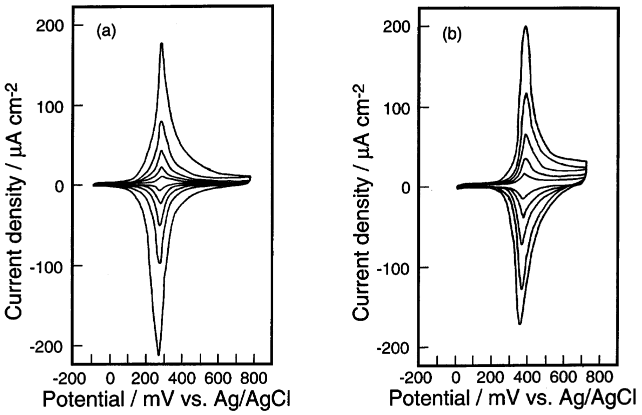

Fig. 1. CVs of the gold electrode modified with the SAM of FcC_6SH measured in (a) 0.1 M HPF_6 aqueous solution and (b) CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate with scan rates of 500, 200, 100, 50, and 20 mV s^{-1}.

sured the cyclic voltammograms (CVs) of a gold electrode modified with the SAM of ferrocenylhexanethiol (FcC_6SH) in aqueous and dichloromethane (CH_2Cl_2) solutions containing various anions such as ClO_4^-, PF_6^- and HSO_4^- (or SO_4^{2-}). We also observed the CVs in the ferrocene dissolved CH_2Cl_2 solutions containing these anions. Based on these results, we discussed the anion effects on the electrochemical characteristics of the ferrocene moiety fixed into the SAM in the aqueous and CH_2Cl_2 solutions.

2. Results and discussion

Fig. 1 shows the typical CVs of the gold electrode modified with the SAM of FcC_6SH measured in (a) aqueous solution and (b) CH_2Cl_2 at various scan rates. In all cases, symmetrical waves due to the redox of the Fc/Fc^+ couple were observed around 200–600 mV (vs. Ag/AgCl), depending on the solvent and the electrolyte (Table 1). In aqueous solutions, the redox potentials of Fc/Fc^+ shifted more positively in the order of PF_6^-, ClO_4^-, and SO_4^{2-} (HSO_4^-). The results of ClO_4^- and SO_4^{2-} (HSO_4^-) are in agreement with the one reported previously [6]. Contrary to the results in the aqueous solutions, the redox potentials of Fc/Fc^+ shifted more negatively in the order of PF_6^-, ClO_4^- and HSO_4^- in CH_2Cl_2. Almost linear relationships between the anodic peak current density and scan rate were observed for all cases, indicating that the current observed in the present study is due to the redox reaction of Fc/Fc^+ fixed on the gold electrode. The surface concentration of FcC_6SH estimated from the integrated anodic charge of these redox peaks was almost the same for all cases of ca. 5.0×10^{-10} mol cm^{-2} ($= 3.0 \times 10^{14}$ molecules cm^{-2}), which was in good agreement with our previous results [6,7].

Table 1
Redox potentials of Fc/Fc^+ couples

Anion [a]	Homogeneous [b] CH_2Cl_2	SAM	
		CH_2Cl_2	Aqueous
PF_6^-	525	460	285
ClO_4^-	495	430	335
HSO_4^-	480	320	480 [c]

[a] The concentration of anion was constant in all the cases to be 0.1 M.

[b] The concentration of ferrocene was constant in all the homogeneous solutions to be 1 mM.

[c] In the case of aqueous solution, electrolyte solution was 0.05 M H_2SO_4.

The electrochemical characteristics of ferrocene dissolved in CH_2Cl_2 containing both 1 mM Fc and 0.1 M ClO_4^-, PF_6^-, or HSO_4^- were also measured for comparison. The redox potentials of Fc/Fc^+ in CH_2Cl_2, which are shown in Table 1, are in good agreement with the literature values [1,12]. The redox potential depended only slightly on the anion and shifted more positively in the order of HSO_4^-, ClO_4^- and PF_6^-.

The redox process of dissolved ferrocene is believed to be expressed by:

$$Fc \rightarrow Fc^+ + e^- \quad (1)$$

In this case, the anion should not affect the redox potential. The small anion effect on the redox potential indicates the small degree of ion-pair formation between Fc^+ and anion in solution, which makes the redox potential more positive, as described below.

When the ferrocene moiety in the FcC_6SH SAM becomes Fc^+ upon oxidation, the anions are required to compensate the electric charge on the gold surface and ion-pairs are formed as having already been well proved [6,11]. Thus, the redox reaction of the ferrocene moiety in the SAM can be described as follows:

$$–Fc + X_s^- \rightarrow –Fc^+X^- + e^- + \text{solv.} \quad (2)$$

where $–Fc$ and $–Fc^+$ are the reduced and oxidized states, respectively, of a ferrocene moiety in the FcC_6SH SAM, X_s^- is a solvated anion, $–Fc^+X^-$ is an ion-pair between Fc^+ and the attached anion, X^-, and solv. is a solvent molecule. This electrochemical reaction (2) can be finally divided into three processes [13,14]:

$$X_s^- \rightarrow X^- + \text{solv.} \quad (3)$$

$$–Fc \rightarrow –Fc^+ + e^- \quad (4)$$

$$–Fc^+ + X^- \rightarrow –Fc^+X^- \quad (5)$$

Therefore, when the anion effect on the redox potential was discussed, the energetics of reactions (3) and (5), i.e. the desolvation energy of the anion ($-\Delta G^\circ_{\text{solv.}}$) and the formation energy of the ion-pair ($\Delta G^\circ_{\text{form.}}$), should be considered for the SAM modified electrodes as follows:

$$\Delta E = \frac{-(-\Delta\Delta G^{\circ}_{\mathrm{solv.}}) - \Delta\Delta G^{\circ}_{\mathrm{form.}}}{nF} \tag{6}$$

where ΔE, $-\Delta\Delta G^{\circ}_{\mathrm{solv.}}$ and $\Delta\Delta G^{\circ}_{\mathrm{form.}}$ are the differences of the redox potential, of the desolvation energy, and of the formation energy of the ion-pair, respectively, between the anions used as electrolytes, n is the number of charge (= 1, in the present study), and F is the Faraday constant.

As a classical theory [13,14], the change in the Gibbs free energy upon solvation of an ion, $\Delta G^{\circ}_{\mathrm{solv.}}$, is known to be approximately equal to the difference between its potential energy in vacuum and in solution, i.e.:

$$\Delta G^{\circ}_{\mathrm{solv.}} = -Nz^2e^2(1-1/\varepsilon)/r \tag{7}$$

where N is Avogadro's number, e is the elementary electric charge, ε is the dielectric constant, and r is the radius of the ion. Based on the ε of water (78.4) and CH_2Cl_2 (8.93) [15], $\Delta G^{\circ}_{\mathrm{solv.}}$ in an aqueous solution should be larger than that in CH_2Cl_2. However, there was no contribution of the structural changes in the ion and solvent, i.e. the entropy term, in Eq. (4). Although many new types of theoretical calculations about $\Delta G^{\circ}_{\mathrm{solv.}}$ were reported [13,14], generally because the anions are solvated in aqueous solutions more than the cations and the cations are solvated in organic solution more than the anions [13], we postulated here that $\Delta G^{\circ}_{\mathrm{solv.}}$ of the various anions is one of the key factors to explain the anion effect on the redox potential in the aqueous solutions, but it can be negligible in CH_2Cl_2.

For the SAM modified electrodes in CH_2Cl_2, when we discuss the anion effect on the redox potential, we should consider only $\Delta G^{\circ}_{\mathrm{form.}}$ because the contribution of $-\Delta G^{\circ}_{\mathrm{solv.}}$ to this anion effect should be negligibly small in CH_2Cl_2 as mentioned above. Although $\Delta G^{\circ}_{\mathrm{form.}}$ includes both the electrostatic and van der Waals interactions between Fc^+ and the anion, the former interaction should be much larger than the latter, and then, we consider only the former to explain the anion effect on the redox potential at the FcC_6SH SAM modified Au(111) electrodes in CH_2Cl_2. The electrostatic interaction, W_E, can be given by:

$$W_{\mathrm{E}} = \frac{q_{\mathrm{Fc^+}} q_{\mathrm{anion}}}{2\pi\varepsilon_0\varepsilon d} \tag{8}$$

where, $q_{\mathrm{Fc^+}}$ and q_{anion} are the number of charge of Fc^+ (+1) and the anion (−1), respectively, and d is the distance between Fc^+ and the anion. Thus, the smaller the r, the larger the W_E, i.e. the larger the $\Delta G^{\circ}_{\mathrm{form.}}$ value. According to the literature values for the thermochemical radius (ClO_4^-, $r = 2.36$ Å; HSO_4^-, $r = 2.06$ Å) and the ionic radius (P^{5+}, $r = 0.34$ Å; F^-, $r = 1.36$ Å; Cl^-, $r = 1.81$ Å; S^{2-}, $r = 1.84$ Å) [14], we can estimate the order of the anion size as $PF_6^- > ClO_4^- > HSO_4^-$, i.e. the order of the electrostatic interaction with Fc^+, i.e. $\Delta G^{\circ}_{\mathrm{form.}}$, should be $HSO_4^- > ClO_4^- > PF_6^-$. Thus, the redox potential shifted more positive in the order of HSO_4^-, ClO_4^- and PF_6^- in CH_2Cl_2. As an example, the redox potential for HSO_4^- was compared with that for ClO_4^-. When the r values of a ferrocene ring are 0.83 Å, which is the ionic radius of Fe^{2+}, or 1.5 Å, which is the radius of the cyclopentadienyl ring of ferrocene, ΔE becomes ca. −105 and −70 mV, respectively. The former value matches well with the observed value (−110 mV), indicating that the anions are placed much closed to Fc^+ when the ion-pair formed. When a value of 0.83 Å was used as the r value of the ferrocene ring, we can estimate the r of PF_6^- from the observed ΔE (−30 mV) to be 2.49 Å. This value is reasonable as concerned with the literature values described above.

For the SAM modified electrodes in aqueous solutions, using the r value of PF_6^- estimated above, the ΔE between PF_6^- and ClO_4^- was calculated from Eq. (8) to be only −3 mV and the direction of the potential shift was different from the observed value (+50 mV). In this case, we can neglect the contribution of $\Delta E_{\mathrm{form.}}$ and we should consider the contribution of the desolvation energy, $-\Delta G^{\circ}_{\mathrm{solv.}}$, as mentioned above. According to Eq. (7), $-\Delta G^{\circ}_{\mathrm{solv.}}$ depends not only on the size of the anions but also on the charge number. The smaller and the larger the size of the anion and the charge number, respectively, the larger the $-\Delta G^{\circ}_{\mathrm{solv.}}$, i.e. the more difficult it is to release the hydrated water molecules from the anion, and then, the more positively the redox potential shifted in the order of PF_6^-, ClO_4^-, and SO_4^{2-}. As an example, using the literature values of $-\Delta G^{\circ}_{\mathrm{solv.}}$ (ClO_4^-, 254.4 kJ mol^{-1}; SO_4^{2-}, 676.1 kJ mol^{-1}) [13], we can calculate the values of ΔE between ClO_4^- and SO_4^{2-} to be +4.4 V, which is the same potential shift direction as is much larger than the observed value (+145 mV). This large discrepancy between the calculated and observed values should be due to the ratio of SO_4^{2-} and HSO_4^- placed at the interface due to the pK_a value of the following reaction:

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-} \tag{9}$$

should be different from that in the bulk. Another possible reason for the discrepancy is the difference in the values of $-\Delta G^{\circ}_{\mathrm{solv.}}$ in the bulk solution and at the interface because ε at the interface should be different from that in the bulk.

In conclusion, based on the above results, the desolvation energy of the anion and the electrostatic interaction between the ferricenium cation and the anion affected the shifts of the redox potential for the ferrocene moiety in the SAM. More details about the anion and solvent effects on the redox potential and kinetics in the organic solutions are now under investigation.

3. Experimental

3.1. Materials

Ferrocenylhexanethiol (FcC_6SH) was synthesized by previously reported procedures [6]. Ultrapure water was obtained using a Milli-Q water purification system (Yamato, WQ-500). Suprapure grade CH_2Cl_2 used as the solvent was obtained from Wako Pure Chemicals and was distilled twice before use. $HClO_4$ (suprapure reagent grade), H_2SO_4 (suprapure reagent grade), hexane (reagent grade), and EtOH (reagent grade) were obtained from Wako Pure Chemicals, HPF_6 (reagent grade) and tetrabutylammonium hexafluorophosphate (reagent grade) were from Aldrich, and tetrabutylammonium perchlorate (electrochemical grade) and tetrabutylammonium hydrogen sulfate (electrochemical grade) were from Nacalai Tesque and they were used without further purification. The gold wire ($>99.95\%$, $\phi = 0.8$ mm) was obtained from Nilaco Co. The pure Ar gas (99.99%) was obtained from Air Water.

3.2. Sample preparation

The gold single crystal used as a substrate was prepared by Clavilier's method [16] from a gold wire, by cutting to expose the (111) face, by mechanically polishing, and by annealing at 800 °C for 10 h in an electric furnace under pure Ar atmosphere. Prior to the surface modification, the gold substrate was annealed by a hydrogen–oxygen flame for a few seconds, and then, quenched in Ar saturated Milli-Q water. Surface modification of the gold substrate was carried out by dipping the substrate into hexane containing 1 mM FcC_6SH for 12 h at room temperature. After the modification, the sample was separately washed with hexane, EtOH, and pure water.

3.3. Electrochemical measurements

The electrolyte solutions were prepared using ultrapure water or distilled CH_2Cl_2 as the solvent and using $HClO_4$, HPF_6, H_2SO_4, $TBAClO_4$, $TBAHSO_4$, or $TBAPF_6$ as the electrolyte. Prior to the electrochemical measurements, the electrolyte solutions were deaerated by passing pure Ar through them for more than 1 h. A three-electrode cell was used for the electrochemical measurements. Ag/AgCl (saturated NaCl) and Pt wire were used as the reference and counter electrodes, respectively. The hanging meniscus method was employed. The electrode potential was controlled by a potentiostat (Hokuto Denko, HA-151), external potential modulation was provided by a function generator (Hokuto Denko, HB-111), and a CV was recorded using an $X-Y$ recorder (Graphtec, WX-1200). The real surface area of the Au(111) electrode was estimated from the reduction charge of gold oxide.

Acknowledgements

This work was partially supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

References

[1] A. Togni, T. Hayashi, Ferrocene, VCH, New York, 1995.
[2] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.
[3] A. Ulman, An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly, Academic Press, New York, 1991.
[4] H.O. Finklea, in: A.J. Bard, I. Rubinstein (Eds.), Electroanalytical Chemistry, vol. 19, Marcel Dekker, New York, 1996.
[5] C.E.D. Chidsey, C.R. Bertozzi, T.M. Putvinski, A.M. Mujsce, J. Am. Chem. Soc. 112 (1990) 4301.
[6] K. Uosaki, Y. Sato, H. Kita, Langmuir 7 (1991) 1510.
[7] K. Uosaki, Y. Sato, H. Kita, Electrochim. Acta 36 (1991) 1799.
[8] M.M. Walczak, D.D. Popenoe, R.S. Deinhammer, B.D. Lamp, C. Chung, M.D. Porter, Langmuir 7 (1991) 2687.
[9] J.J. Hickman, D. Ofer, P.E. Laibinis, G.M. Whitesides, M.S. Wrighton, Science 252 (1991) 688.
[10] J.F. Smalley, S.W. Feldberg, C.E.D. Chidsey, M.R. Linford, M.D. Newton, Y.P. Liu, J. Phys. Chem. 99 (1995) 13141.
[11] S. Ye, T. Haba, Y. Sato, K. Shimazu, K. Uosaki, Phys. Chem. Chem. Phys. 1 (1999) 3653.
[12] W.R. Everett, T.L. Welch, L. Reed, I. Fritsch-Faules, Anal. Chem. 67 (1995) 292.
[13] B.E. Conway, Ionic Hydration in Chemistry and Biophysics, Elsevier, New York, 1981.
[14] G.A. Krestov, Thermodynamics of Solvation, Ellis Horwood, Chichester, 1991.
[15] J.A. Riddick, W.B. Bunger, Organic Solvents, Wiley, New York, 1970.
[16] J. Clavilier, R. Faure, G. Guinet, R. Durand, J. Electroanal. Chem. 107 (1980) 205.