Tetrahedron Letters 50 (2009) 1032–1034

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Redox interaction of sulfonated polyaniline with vanadium(IV) in water

Toru Amaya, Shogo Koga, Toshikazu Hirao *

Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

ARTICLE INFO

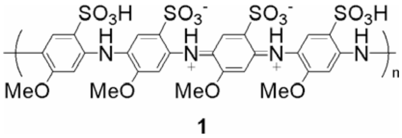
Article history:
Received 14 November 2008
Revised 9 December 2008
Accepted 12 December 2008
Available online 24 December 2008

Keywords:
Redox
Polyaniline
Vanadium

ABSTRACT

The redox interaction between poly(2-methoxyaniline-5-sulfonic acid) (PMAS, emeraldine form) and V(IV) readily occurred to produce the PMAS(red) and V(V) species in an aqueous solution. Notably, molecular oxygen was able to reoxidize PMAS(red) to form the catalytic redox cycle. This redox interaction was effectively observed in basic conditions rather than in acidic ones.

Catalytic oxidation reactions in biological systems depend on efficient multi-redox cycles using molecular oxygen as a terminal oxidant.[1] The construction of such artificial cycles is envisioned to be not only useful in organic reactions, but also important in view of ecological chemistry.[2–4] We have investigated the construction of multi-redox systems based on d,π-conjugation of polyanilines with various metal ions (i.e., Pd(II), Cu(II), and V(III))[5,6] or metal nanoparticles.[7] Their catalytic application has also been demonstrated in some oxidation reactions like the Wacker reaction.[8] The development of such catalytic systems in water is considered to afford ecological redox catalysts. Water-soluble, redox-active, and self-doped fully sulfonated polyaniline, poly(2-methoxyaniline-5-sulfonic acid) (PMAS, emeraldine **1**, Fig. 1),[9] was selected in this study to serve as a redox mediator. Vanadium compounds are known to show various redox behaviors in some aqueous solutions with various ranges of pH.[10] We herein report the redox behavior between V(IV) species and PMAS in an aqueous solution.



1

Figure 1. PMAS, emeraldine **1**.

PMAS emeraldine **1** was presented by Mitsubishi Rayon Co. Compound **1** was deionized through cation-exchange resins before use. The redox interaction was mainly studied by UV–vis spectrometry in various pHs. In the case of pH 8.8, the addition of $VOSO_4$ (10 equiv) to an aqueous solution of PMAS (0.1 mM based on the aniline unit, 1 equiv) immediately decreased the polaron band at 472 nm[11] assignable to a PMAS emeraldine form (Fig. 2b). Concurrently, the new peak appeared at 408 nm. After 1 h, the polaron band was gradually restored over a day with decrease in the peak at 408 nm (Fig. 2b). The isosbestic point was observed at 345 nm in 0–1 h, suggesting the oxidation reaction of V(VI) to V(V) (Fig. 2a). On the other hand, after 2 h, another isosbestic point appeared at 422 nm. It is likely to show the reoxidation reaction process of PMAS(red) **2** to **1** (Fig. 2a). To confirm these redox processes, several experiments were conducted as follows. When the same reaction was carried out under argon, the restoration of the polaron band was not observed even after 16 h. However, once molecular oxygen was bubbled into the reaction mixture, the polaron band was restored with decrease in the peak at 408 nm. These results indicate that the reduction of **1** occurs together with the oxidation of the V(IV) species to the V(V) ones in the beginning of the reaction. The thus-obtained reduced PMAS was then oxidized under molecular oxygen. These redox processes were spectroscopically confirmed by the comparison of the UV–vis spectra using PMAS(red) **2**, which was separately prepared by hydrogenation of **1** (Scheme 1). This reaction was also conducted in a D_2O solution to support the oxidation state of the vanadium species using ^{51}V NMR. The new peak was observed at −576.3 ppm in ^{51}V NMR after stirring for 1 h,[12] which showed the presence of V(V). These findings indicate the formation of a redox cycle in an aqueous solution (Scheme 2). The observed redox interaction might be induced differently, probably due to the presence of the sulfonate moiety in PMAS, from our previous cases in organic media, where the coordination of the quinonediimine moiety of polyaniline contributes to the redox interaction.[5,6]

---

* Corresponding author. Tel.: +81 6 6879 7413; fax: +81 6 6879 7415.
E-mail address: hirao@chem.eng.osaka-u.ac.jp (T. Hirao).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.12.049

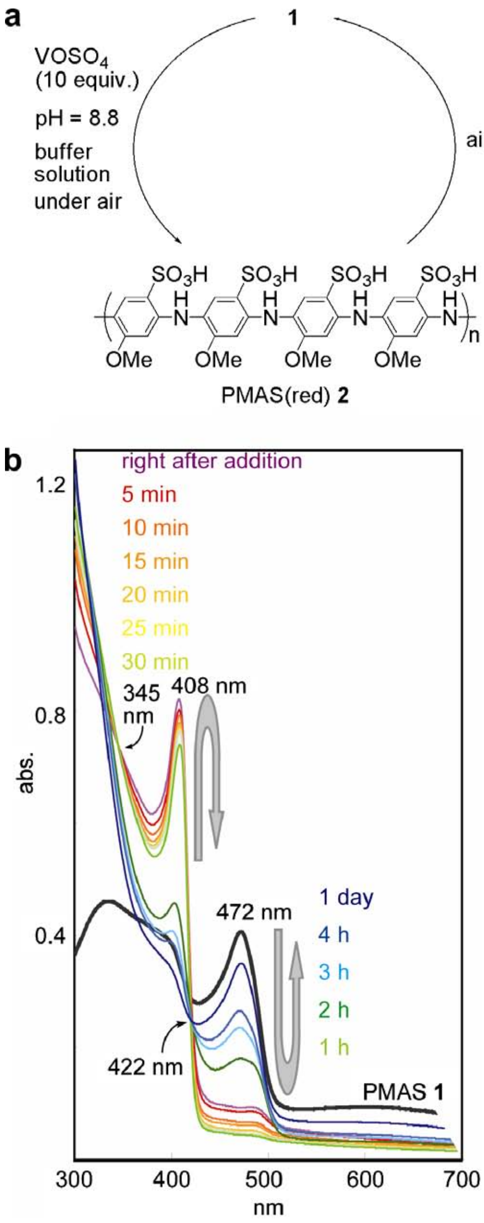
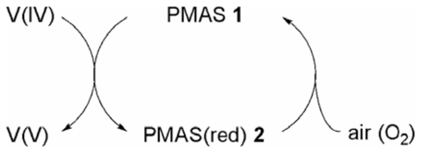


Figure 2. Redox interaction of **1** and $VOSO_4$ at pH 8.8: (a) reaction scheme, (b) time-dependent UV–vis spectra (**1**: 0.1 mM based on the aniline unit).

$$\mathbf{1} \xrightarrow[\text{H}_2\text{O, MeOH, rt, quant.}]{\text{H}_2\text{, Pd/C}} \text{PMAS(red) } \mathbf{2}$$

Scheme 1. Hydrogenation of **1**.

Quantitative determination for V(V) was carried out using ^{51}V NMR to investigate the effect of PMAS as a redox mediator. 10 mol % of PMAS was mixed with $VOSO_4$ at pH 8.8 (concentration of $VOSO_4$: 1.0×10^{-2} mM in a phosphate buffer D_2O solution). The progress of the reaction is shown in Figure 3. After stirring at room temperature for 2 h under air, V(IV) was converted to V(V) in 96% yield, where the turn over number of PMAS was almost 10. On the other hand, the absence of PMAS afforded V(V) species in a low yield (13%). These results clearly indicate that PMAS works as a redox mediator to accelerate the oxidation reaction of V(IV).



Scheme 2. Redox cycle of PMAS.

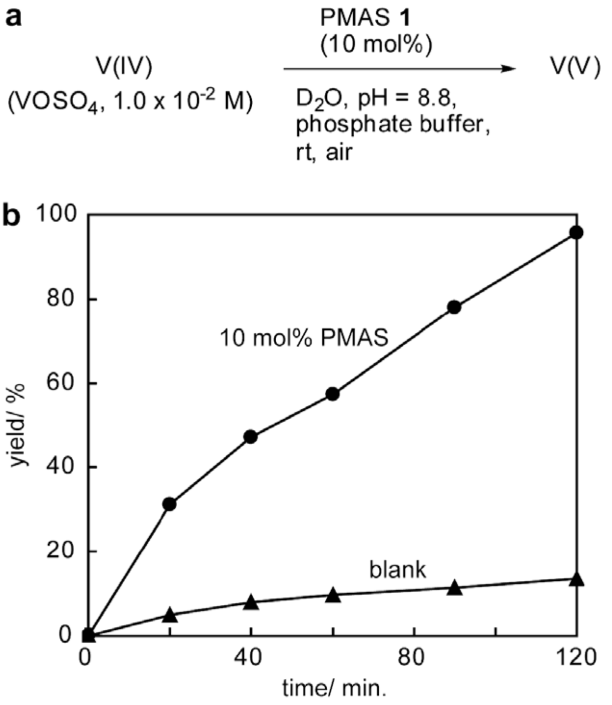


Figure 3. (a) Reaction scheme for the oxidation of V(IV). (b) Graph showing the relationship between the yield of V(V) and time.

The redox interaction of PMAS and V(IV) was further investigated in basic, neutral, and acidic conditions. $VO(acac)_2$ was examined as another vanadium(IV) species. One equivalent of $VO(acac)_2$ was added to an aqueous solution of PMAS (0.1 mM based on the aniline unit, 1 equiv). Figures 4a and b show the UV–vis spectra. In the case of the basic conditions (pH 8.8), a similar trend in the spectral changes was observed as described with $VOSO_4$ in the previous paragraph, while the changes were smaller due to the use of less amount of V(IV) (Fig. 4a). In the neutral conditions, the redox reaction was also observed while the efficiency of the reaction was lower in comparison with that in the basic ones (Fig. 4b). However, the acidic conditions were undesirable for the redox interaction since no significant changes were exhibited around the polaron bands in the UV–vis spectra.

In conclusion, the present study revealed that the redox interaction between **1** and V(IV) readily occurs to produce **2** and V(V) species in an aqueous solution. Notably, molecular oxygen was able to reoxidize **2** to form the redox cycle, which provides the V(V) species. These redox cycles effectively work in the basic conditions rather than in the acidic ones. In many biological systems, redox-active mediators often play an important role to facilitate reoxidation of a reduced form of the transition metal catalyst. Thus-constructed water-soluble redox systems are considered to be addressed as a new class of bio-inspired redox systems. Since high valent vanadium complexes are known to catalyze various oxidation reactions,[13] the catalytic application in water is now in progress.

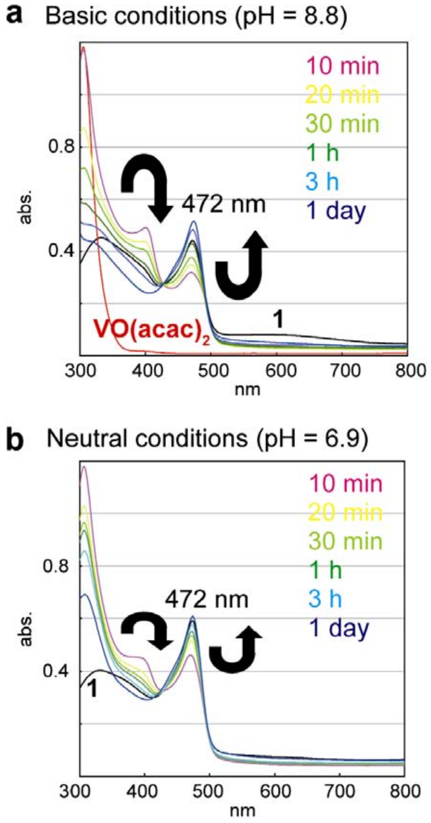


Figure 4. Time-dependent UV–vis spectra of the reactions between **1** and VO(acac)$_2$ at (a) pH 8.8 and (b) pH 6.9.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas 'Advanced Molecular Transformations of Carbon Resources' from the Ministry of Education, Sports, Science and Technology, Japan. Thanks are due to donation of PMAS from Mitsubishi Rayon Co.

References and notes

1. (a) Duester, G. *Biochemistry* **1996**, *35*, 12221–12227; (b) Berg, J. M.; Tymoczko, J. L.; Stryer, L. *Biochemistry*, 5th ed.; W. H. Freeman: New York, 2002.
2. For reviews: (a) Sheldon, R. A.; Arends, I. W. C. E.; Brink, G.-J. T.; Dijksman, A. *Acc. Chem. Res.* **2002**, *35*, 774–781; (b) Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329–2363.
3. For a theoretical study: Deubel, D. V. *J. Am. Chem. Soc.* **2004**, *126*, 996–997.
4. For recent reports: (a) Piera, J.; Narhi, K.; Backvall, J.-E. *Angew. Chem., Int. Ed.* **2006**, *45*, 6914–6917; (b) An, Z.; Pan, X.; Liu, X.; Han, X.; Bao, X. *J. Am. Chem. Soc.* **2006**, *128*, 16028–16029.
5. Hirao, T. *Coord. Chem. Rev.* **2002**, *226*, 81–91.
6. (a) Hirao, T.; Higuchi, M.; Ikeda, I.; Ohshiro, Y. *J. Chem. Soc., Chem. Commun.* **1993**, 194–195; (b) Higuchi, M.; Imoda, D.; Hirao, T. *Macromolecules* **1996**, *29*, 8277–8279; (c) Hirao, T.; Yamaguchi, S.; Fukuhara, S. *Tetrahedron Lett.* **1999**, *40*, 3009–3012; (d) Hirao, T.; Yamaguchi, S.; Fukuhara, S. *Synth. Met.* **1999**, *106*, 67–70; (e) Hirao, T.; Fukuhara, S.; Otomaru, Y.; Moriuchi, T. *Synth. Met.* **2001**, *123*, 373–376; (f) Moriuchi, T.; Bandoh, S.; Miyaishi, M.; Hirao, T. *Eur. J. Inorg. Chem.* **2001**, 651–657; (g) Moriuchi, T.; Miyaishi, M.; Hirao, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3042–3045; (h) Shen, X.; Moriuchi, T.; Hirao, T. *Tetrahedron Lett.* **2004**, *45*, 4733–4736; (i) Moriuchi, T.; Shen, X.; Hirao, T. *Tetrahedron* **2006**, *62*, 12237–12246.
7. (a) Amaya, T.; Saio, D.; Hirao, T. *Tetrahedron Lett.* **2007**, *48*, 2729–2732; (b) Amaya, T.; Nishina, Y.; Saio, D.; Hirao, T. *Chem. Lett.* **2008**, *37*, 68–69; (c) Amaya, T.; Saio, D.; Hirao, T. *Macromol. Symp.* **2008**, *270*, 88–94.
8. (a) Hirao, T.; Higuchi, M.; Hatano, B.; Ikeda, I. *Tetrahedron Lett.* **1995**, *36*, 5925–5928; (b) Higuchi, M.; Yamaguchi, S.; Hirao, T. *Synlett* **1996**, 1213–1214.
9. Shimizu, S.; Saitoh, T.; Uzawa, M.; Yuasa, M.; Yano, K.; Maruyama, T.; Watanabe, K. *Synth. Met.* **1997**, *85*, 1337–1338.
10. Crans, D. C.; Tracey, A. S. The Chemistry of Vanadium in Aqueous and Nonaqueous Solution. In *Vanadium Compounds*; Tracey, A. S., Crans, D. C., Eds.; American Chemical Society: Washington, DC, 1998; p 2.
11. (a) Yamamoto, T.; Ushiro, A.; Yamaguchi, I.; Sasaki, S. *Macromolecules* **2003**, *36*, 7075–7081; (b) Strounina, E. V.; Shepherd, R.; Kane-Maguire, L. A. P.; Wallace, G. G. *Synth. Met.* **2003**, *135–136*, 289–290.
12. ^{51}V NMR spectra were obtained with a JEOL JNM-ECP 400 (105 MHz) spectrometer with VOCl$_3$ as an external standard (0 ppm).
13. Hirao, T. Synthetic Transformation via Vanadium-Induced Redox Reactions. In *Vanadium: The Versatile Metal*; Kustin, K., Pessoa, J. C., Crans, D. C., Eds.; American Chemical Society: Washington, DC, 2007; p 2.