

oxidation, respectively. Experiments in D₂O showed similar results. Movements of a rather large number of solvent molecules with the redox process may indicate the complex nature of monolayer self-assembly/electrolyte interfacial region. More water molecules might be expected to be trapped in the self-assembly/solution interface. Recent EQCM data observed at electrodes modified with osmium polymer complexes also show that a number of water accompany the redox reaction of osmium (III/II) sites.⁸ The same type of EQCM experiments with the anions of ClO₄⁻ and Cl⁻ were performed to find the variation of the number of solvent molecules moving simultaneously with the first redox process of viologen. Equivalent molar mass (*M_{eq}*) was determined to be 240 and 598 for perchlorates and chlorides, respectively. Because the molar masses of the anions are 99.5 (ClO₄⁻) and 35.5 (Cl⁻), *M_{eq}* determined would imply the simultaneous movements of water molecules (*ca.* 8 H₂O for ClO₄⁻ and *ca.* 31 H₂O for Cl⁻) into the self-assembly during oxidation if a unidirectional transport and permselectivity of the film to anions are assumed. The results were again confirmed by separate experiments in D₂O instead of H₂O. Thus the *in situ* mass transport measurements indicate that the self-assembled molecular C₂₂VC₁ films formed on gold surfaces contain water molecules and become compact in the order Cl⁻ < TS⁻ < ClO₄⁻. Buttry recently reported that simultaneous incorporation of anions and solvent water into the electroactive self-assembled monolayers of ferrocenes occurs upon electrochemical oxidation of ferrocenes to ferrocenium ions.⁹ Therefore, it appears that self-assembled molecular films on electrode surfaces contain a number of solvent water molecules although they are believed to be firmly organized based on the blocking properties for the reduction of Ru(NH₃)₆³⁺ and believed to be hydrophobic because their formation is mainly due to intermolecular hydrophobic interactions. Further EQCM studies are in progress with the self-assembly of asymmetric viologens.

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References

- Lee, C.-W.; Oh, M.-K.; Jang, J.-M. *Langmuir*, **1993**, *9*, 1934 and references therein.
- Li, J.; Kaifer, A. E. *Langmuir* **1993**, *9*, 591 and references therein.
- Cotton, T. M.; Kim, J.-H.; Uphaus, R. A. *Microchem. J.* **1990**, *2*, 44.
- Lee, C.-W.; Bard, A. J. *Chem. Phys. Lett.* **1990**, *170*, 57.
- Self-assembled (physisorbed) films at electrodes should be differentiated from surface-bonded (chemisorbed) films, where covalent bonds between the functional groups of adsorbates and electrode surfaces are formed spontaneously.
- Okajima, T.; Sakurai, H.; Oyama, N.; Tokuda, K.; Ohsaka, T. *Electrochim. Acta.* **1993**, *38*, 747.
- De Long H. C.; Buttry, D. A. *Langmuir* **1990**, *6*, 1319.
- Kelly, A. J.; Oyama, N. *J. Phys. Chem.* **1991**, *95*, 957.

- De Long, H. C.; Donohue, J. J.; Buttry, D. A. *Langmuir* **1991**, *7*, 2196.
- Gomez, M.; Li, J.; Kaifer, A. E. *Langmuir* **1991**, *7*, 1797.

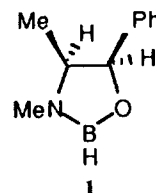
Asymmetric Borane Reduction of Ketoxime O-Trimethylsilyl Ethers Mediated by a Chiral 1,3,2-Oxazaborolidine Derived from (-)-Ephedrine

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One of the most convenient methods for the preparation of optically active primary amines is asymmetric reduction of ketoxime derivatives. However such reduction has been sparse and only very limited success has been achieved.¹ Very recently, we undertook the comparison study of asymmetric borane reduction of some representative ketimines and ketoxime ethers possessing C=N bond mediated by various chiral oxazaborolidines.² In this study, we found that a chiral oxazaborolidine **1** derived from (-)-ephedrine afforded the best result to give a high optical induction (90% ee) for acetophenone oxime O-trimethylsilyl ether **2d**. This result led us to investigate the asymmetric borane reduction of O-trimethylsilyl ethers **2** of other aliphatic and aromatic ketoximes, such as 2-butanone oxime **2a**, 4-methyl-2-pentanone oxime **2b**, 3-methyl-2-butanone oxime **2c**, propiophenone oximes **2e**, isobutyrophenone oxime **2f** pivalophenone oxime **2g** and tetralone oxime **2h**, using this reagent. All of the O-trimethylsilyl ethers of ketoximes examined were prepared by treatment of the corresponding ketoximes with chlorotrimethylsilane in the presence of triethylamine in THF.²



The reductions were carried out with 1 equiv of borane-THF in the presence of 1 equiv of **1** in THF at room temperature. Thus, the reductions of O-trimethylsilyl ethers of unhindered aliphatic ketoxime **2a** proceeded smoothly to give the corresponding primary amines **3a** in a high chemical yield with 38% ee. However, the reduction of O-trimethylsilyl ethers of relatively hindered aliphatic ketone oximes **2b-2c** proceeded at a somewhat slower rate to provide **3b** and **3c** with optical yields of 44% ee and 66% ee, respectively, showing the increase of optical induction by the variation of the steric size of R in MeCR=NOTMS from Et→i-Bu→i-Pr. The aromatic ketoxime derivatives **2d-2f** and **2h**

