CHEMCOMM Communication
www.rsc.org/chemcomm

First example of electroassisted biomimetic activation of molecular oxygen by a (salen)Mn epoxidation catalyst in a room-temperature ionic liquid

Laurent Gaillon[a] and Fethi Bedioui*[b]

[a] *Laboratoire d'Electrochimie et Chimie Analytique, UMR CNRS-ENSCP n° 7575, UPMC, Bat F., 4 place Jussieu, 75252 Paris cedex 05, France*
[b] *ENSCP, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France. E-mail: bedioui@ext.jussieu.fr*

Received (in Cambridge, UK) 19th March 2001, Accepted 2nd July 2001
First published as an Advance Article on the web 19th July 2001

A first example of electroassisted activation of molecular oxygen by Jacobsen's epoxidation catalyst in an ionic liquid at room temperature has been achieved and showed the formation of the postulated high-valent manganese–oxo active intermediate.

Over the past few years, room temperature ionic liquids have re-attracted a wide range of sections of chemistry and generated much excitement and interest for various applications.[1] This renewed vigour is principally linked to the fact that these liquids have simple physical properties making them 'green friendly solvents' (easy to recycle, non-volatile and non-flammable). Thus, they offer potential alternatives for a large variety of disciplines, especially organic and inorganic chemistries. Recently, the discovery of enzyme activity in these media[1c] extends their potential use to bioinorganic applications. This context fits well with the desire to mimic enzymatic systems involving synthetic models (porphyrins and Schiff bases), especially for monooxygenases of the cytochrome P-450 family.[2]

Indeed, analysis of comparative studies dealing with the selectivity, efficiency, stability and recovery for both synthetic models and natural systems have shown that efficiency arises from the control of the environment of the enzyme active site and the development of practical immobilisation methods for catalysts, such as clay-intercalation,[3] zeolite-encapsulation,[4] covalent attachment to an organic polymeric matrix[5] and the use of two-phase systems.[6] Although relatively few efficient examples have been reported they constitute an important contribution to the development of efficient chemical systems operating according the catalytic cycle of substrate oxidation by cytochrome P-450, which involves a supposed high valent metal–oxo intermediate.[7] In the last decade, we have shown the first and rare examples involving electroassisted activation of molecular oxygen to generate metal–oxo active species for biomimetic oxidation of various hydrocarbons by immobilised enzyme models.[8,9]

Recently, Song and Roh[10] reported on the use of ionic liquids as practical recycling media for Jacobsen's catalyst {[*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine)]-manganese(III) chloride, the so-called chiral (salen)Mn epoxidation catalyst and denoted here **[Mn(III)]$^+$**, Fig. 1}, for the asymmetric epoxidation of alkenes by aqueous NaOCl (as the oxidant) in the air-and moisture-stable ionic liquid [bmim][PF_6] at 0 °C, ([bmim]$^+$ = 1-butyl-3-methylimidazolium cation, Fig. 1). Our interest in electroassisted biomimetic reactions encourages us to explore a further extension of our clean chemistry concept, involving molecular oxygen and electrochemistry, into the field of a non-aqueous and polar two-phase process alternative, to provide not only simple recycling of the catalyst without modification of its structure, but also an increase in its activity. Herein, we report for the first time the electrochemical analysis of the biomimetic activation of molecular oxygen with the electrochemically reduced catalyst **[Mn(III)]$^+$** (in the presence of benzoic anhydride and 1-methylimidazole) in the ionic liquid [bmim][PF_6]. This study constitutes the first approach demonstrating the possible existence of the key steps responsible for the electroassisted formation, from molecular oxygen, of the highly reactive [Mn(V)=O]$^+$ manganese–oxo intermediate in these conditions.

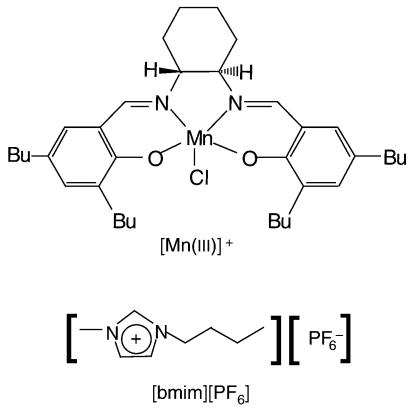


Fig. 1 Structures of **[Mn(III)]$^+$** and [bmim][PF_6].

Electrochemical experiments were carried out at a vitreous carbon electrode of area 0.07 cm^2 in [bmim][PF_6], conveniently prepared,[11] in the presence of **[Mn(III)]$^+$** catalyst and 1-methylimidazole (in the presence/absence of benzoic anhydride and molecular oxygen).† Fig. 2(a) shows the cyclic voltammogram of **[Mn(III)]$^+$** in a deaerated solution of the ionic liquid [bmim][PF_6] containing 1-methylimidazole. It exhibits a pair of well-defined peaks at $E \approx -0.460$ V *vs.* SCE corresponding to

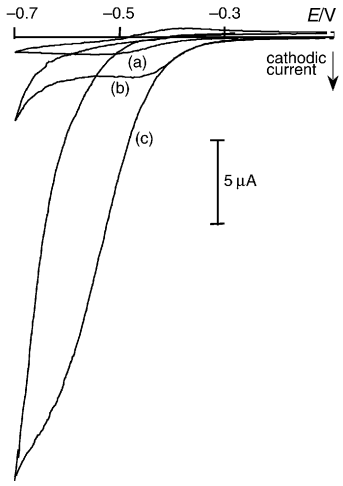


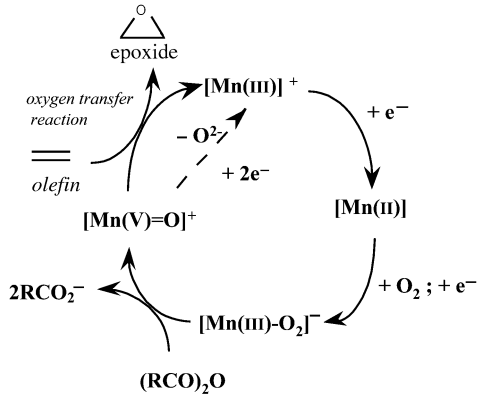
Fig. 2 Cyclic voltammograms of **[M(III)]$^+$** catalyst (2 mM) in [bmim][PF_6] ionic liquid in presence of 1-methylimidazole (10 mM) at room temperature (potential scan rate = 50 mV s^{-1}): (a): deaerated solution; (b) in the presence of molecular oxygen (saturated solution); (c) in the presence of benzoic anhydride (0.1 M) and molecular oxygen.

 DOI: 10.1039/b102526k

the reversible Mn^{III}/Mn^{II} redox process, by reference to the electrochemical behaviour of similar models in several organic solvents.[9,12,13] This was confirmed by rotating disk electrode voltammetry (data not shown). In presence of molecular oxygen, three main features related to the Mn^{III}/Mn^{II} reduction peak appear [Fig. 2(b)]: (i) its potential shifts to a higher potential value, *(ii)* its intensity is enhanced and *(iii)* its associated re-oxidation peak disappears. Such modification of the cyclic voltammogram is similar to that previously reported with related manganese catalysts under various conditions (dissolved or immobilised on solid supports and in organic solvents).[8,9,12,13] and is consistent with the first two steps of the catalytic cycle shown in Scheme 1.[12] Indeed, the reductive peak observed in Fig. 2(b) is representative of the reaction between the catalyst **[Mn(III)]**$^+$ (in the presence of 1-methylimidazole as an axial coordinating ligand, not shown in the cycle of Scheme 1) and molecular oxygen O_2, leading to a doubly reduced complex–oxygen adduct $[Mn–O_2]^-$, that can be interpreted as an 'electron transfer–chemical step–electron transfer' process.[9,12,13]

Fig. 2(c) shows the cyclic voltammogram of **[Mn(III)]**$^+$ in $[bmim][PF_6]$ containing both 1-methylimidazole and benzoic anhydride upon addition of molecular oxygen. A very large enhancement of the Mn^{III}/Mn^{II} reduction current peak is clearly observed. By reference to previously reported studies of similar complexes in several organic solvents, the modification of the cyclic voltammogram shows the occurrence of the expected reaction of the above mentioned $[Mn–O_2]^-$ adduct with anhydride $[(RCO)_2O]$ to give the high-valent manganese–oxo $[Mn(V)=O]^+$ intermediate, followed by its reduction and the steady state electrocatalytic regeneration of **[Mn(III)]**$^+$ (Scheme 1).[8,9,12,13] It is important to note that this reduction occurs competitively with the reaction of transfer of an oxygen to hydrocarbon in solution. However, we observed that the inclusion of olefin (*cis*-cyclooctene) did not produce a significant modification of the voltammograms, implying that the reaction is fast enough to be competitive with the rate of formation of the oxo complex.[9a,12] Finally, we have verified that the direct reduction of molecular oxygen takes place at *ca.*−0.8 V *vs.* SCE, outside the potential range investigated in this study, and that the presence of benzoic anhydride does not induce any electrochemical interference. Rotating disk voltammetry confirms all the above observations (data not shown).

In summary, this result shows for the first time the electroassisted biomimetic activation of molecular oxygen by Jacobsen's epoxidation catalyst in an ionic liquid and clearly demonstrates the possible existence of the key steps responsible for the formation of the highly reactive $[Mn(V)=O]^+$ manganese–oxo intermediate in the ionic liquid $[bmim][PF_6]$. This unique observation, combined with the immobilisation of the catalyst by using the ionic liquid, allows us to confidently explore this clean chemistry concept involving molecular oxygen and electrochemistry. Detailed studies are now in progress to extend this investigation to the preparative scale, for the epoxidation of selected olefins which may offer, for the first time to our knowledge, a possible extension of electrocatalysis and electrosynthesis to ionic liquid solvents.



Scheme 1 Proposed scheme for the electroassisted activation of molecular oxygen by **[M(III)]**$^+$ catalyst for olefin epoxidation reaction.

We are grateful to Prof. P. Letellier and Dr J. Devynck for helpful discussion and interest in this work.

Notes and references

† *Representative procedure* for the electrochemical study: all electrochemical studies were performed with a standard three-electrode potentiostatic system (Taccussel). The potentials are referred to an aqueous saturated Calomel electrode, (SCE), placed in a separate compartment. All the experiments were performed under atmospheric pressure and at ambient temperature. Jacobsen's catalyst was purchased from Aldrich and used as received while the ionic liquid $[bmim][PF_6]$ was prepared and purified as previously reported.[11]

1 Reviews: (*a*) T. Welton, *Chem. Rev*., 1999, **99**, 2071; (*b*) M. Freemantle, *C&EN*, 2000, 37; (*c*) M. Freemantle, *C&EN*, 2001, 21.
2 D. Mansuy and P. Battioni, *Cytochrome P-450 Model Systems in Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker, New York, 1994, p. 99.
3 For review: F. Bedioui, *Coord. Chem. Rev*., 1995, **144**, 39 and references therein.
4 N. Herron, *J. Coord. Chem*., 1988, **19**, 25; R. Parton, D. De Vos and P. A. Jacobs, *Enzyme Mimicking with Zeolites in Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*, ed. G. A. Derouane, Kluwer Academic Publishers, Amsterdam, 1992, p. 555; K. J. Balkus Jr., A. K. Khanmamedov, K. M. Dixon and F. Bedioui, *Appl. Catal*., 1996, **143**, 159 and references therein.
5 F. Bedioui, J. Devynck and C. Bied-Charreton, *Acc. Chem. Res*., 1995, **28**, 30 and references therein; F. Bedioui, J. Devynck and C. Bied-Charreton, *J. Mol. Catal*., 1996, **113**, 3 and references therein.
6 G. Oehme, *Catalyst Immobilization: Two-Phase Systems*, in *Comprehensive Asymmetric Catalysis III*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springler-Verlag, Berlin–Heidelberg–New York, 1999, p. 1378.
7 *Cytochrome P-450: Structure, Mechanism and Biochemistry*, ed. P. R. Ortiz de Montenallo, Plenum Press, New York, 1986; B. Meunier, *Chem. Rev*., 1992, **92**, 1411.
8 L. Gaillon, F. Bedioui, P. Battioni and J. Devynck, *J. Mol. Catal*., 1993, **78**, L23.
9 (*a*) F. Bedioui, S. Gutierrez Granados, C. Bied-Charreton and J. Devynck, *New J. Chem*., 1991, **15**, 939; (*b*) F. Bedioui, S. Gutierrez Granados, L. Gaillon, C. Bied-Charreton and J. Devynck, *Stud. Surf. Sci. Catal*., 1991, **66**, 221; (*c*) F. Bedioui, P. Moisy, J. Devynck, L. Salmon and C. Bied-Charreton, *J. Mol. Catal*., 1989, **56**, 267; (*d*) P. Moisy, F. Bedioui, Y. Robin and J. Devynck, *J. Electroanal. Chem*., 1988, **250**, 191.
10 C. E. Song and E. J. Roh, *Chem. Commun*., 2000, 837.
11 J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun*., 1998, 1765.
12 S. E. Creager, S. Raybuck and R. W. Murray, *J. Am. Chem. Soc*., 1986, **108**, 4225; C. P. Horwitz, S. E. Creager and W. R. Murray, *Inorg. Chem*., 1990, **29**, 1006.
13 S. Gutierrez Granados, F. Bedioui and J. Devynck, *Electrochim. Acta*, 1993, **38**, 1747.