Oxygen and proton reduction by decamethylferrocene in non-aqueous acidic media†

Bin Su,a İmren Hatay,ab Pei Yu Ge,a Manuel Mendez,a Clemence Corminboeuf,c Zdenek Samec,d Mustafa Ersozb and Hubert H. Girault*a

Received (in Cambridge, UK) 18th January 2010, Accepted 3rd March 2010
First published as an Advance Article on the web 18th March 2010
DOI: 10.1039/b926963k

Experimental studies and density functional theory (DFT) computations suggest that oxygen and proton reduction by decamethylferrocene (DMFc) in 1,2-dichloroethane involves protonated DMFc, DMFcH+, as an active intermediate species, producing hydrogen peroxide and hydrogen in aerobic and anaerobic conditions, respectively.

O2 reduction by ferrocene and its derivatives in organic media in the presence of an acid, such as trichloroacetic and trifluoroacetic acids and perchloric acid, has been known for many years.1–5 Recently, O2 reduction has also been studied in biphasic systems composed of an organic solvent containing a ferrocene derivative in contact with an aqueous inorganic acid solution containing a very lipophilic anion.6–8 At such liquid–liquid interfaces, O2 reduction takes place by involving the lipophilic electron donors i.e. ferrocene derivatives located in the organic phase and aqueous protons. Moreover, it has been found that in the same biphasic system the electron-rich decamethylferrocene (DMFc) can also reduce aqueous protons under anaerobic conditions, leading to the evolution of hydrogen.9 In both cases, the reaction has been proposed to proceed in two steps: first a heterogeneous proton transfer facilitated by DMFc from the aqueous to the organic phase as observed by voltammetry experiments at liquid–liquid interfaces, followed by a homogenous proton/oxygen reduction in the organic phase, the mechanism of which being yet unresolved. In this communication, we present experimental results for oxygen/proton reductions by DMFc in bulk 1,2-dichloroethane (DCE) in the presence of organic acids. In the case of oxygen reduction, DFT computations support a reaction pathway involving protonated DMFc, DMFcH+, as an intermediate species, which reacts with oxygen to produce hydrogen peroxide.

Fig. 1a illustrates an experiment performed in DCE under aerobic conditions. A dilute solution of DMFc appeared yellow, to which addition of an acid, hydrogen tetrakis(pentafluorophenyl)borate (HTB),§ led to an immediate colour change to bright green. In the UV-visible spectrum, the absorption band of DMFc centered at 425 nm is replaced by a strong band of DMFc+ at 779 nm. Moreover, by shaking the green organic solution with pure water and then by titrating this aqueous phase with sodium iodide (NaI), triiodide was detected with a spectroscopic signature at 286 nm and 330 nm. Triiodide was generated by oxidation of iodide by H2O2.7 These results suggest the occurrence of oxygen reduction to H2O2 by DMFc in DCE in the presence of the organic acid:

$$2\text{DMFc} + \text{O}_2 + 2\text{H}^+ + \text{TB} \rightarrow 2\text{DMFc}^+\text{TB}^- + \text{H}_2\text{O}_2$$ (1)

However, only 0.03 mM of H2O2 was detected, an amount which is about five times less than that of DMFc+ produced (1.5 mM). This indicates a much lower yield than the stoichiometric value for H2O2. One possible reason is the further reduction of H2O2 by DMFc to finally produce water. Indeed, in biphasic systems, the yield of H2O2 can reach 40% as its extraction to water competes with further reduction.7 Another possible reason for this low yield is the competing proton reduction. The latter hypothesis was investigated by performing the same experiment under anaerobic conditions.

Fig. 2 shows gas chromatograms obtained on a Perkin-Elmer gas chromatograph (Clarus 400) equipped with packed 5 Å molecular sieves, 80/100 mesh, using a TCD detector and argon as the carrier gas. In anaerobic conditions (Fig. 2a) a clear H2 signal can be observed confirming similar results to
those obtained in biphasic systems, whereas some small amount of \( \text{H}_2 \) can still be observed in aerobic conditions (Fig. 2b) suggesting that proton and oxygen reductions do compete, but that hydrogen production cannot account for the low \( \text{H}_2\text{O}_2 \) generation yield. It must be stressed that the solution turns green within minutes in the presence of oxygen whereas it takes a couple of hours in anaerobic conditions.

Previous studies at liquid–liquid interfaces suggested that in both cases the initial step is the protonation of \( \text{DMFc} \) leading to the formation of \( \text{DMFcH}^+ \). The protonation of ferrocene was reported to result in a tilting of the rings thus facilitating the binding of \( \text{O}_2 \) at the \( \text{Fe} \) atom directly, which is then followed by oxygen reduction. Considering that insertion of triplet \( \text{O}_2 \) is spin-forbidden, Fomin proposed the formation of an hydrogen-bond intermediate, \( \text{O}_2 \) being sandwiched between two protonated ferrocenes followed by the generation of \( \text{H}_2\text{O}_2 \) by concerted breakdown of two \( \text{Fe}–\text{H} \) and formation of two \( \text{H}–\text{O} \) bonds. The present DFT computations do not support the hypothesis that triplet molecular oxygen \( \text{O}_2 \) coordinates to the iron atom through a spin-forbidden mechanism or inserts into the Fe–H bond. Instead, the present computations show that \( \text{O}_2 \) can approach the activated hydride directly via a delocalized triplet (diradical) transition state \( [\text{DMFc}–\text{O}_2] \) (Scheme 1) with an activation barrier of 15 kcal mol\(^{-1}\) in the gas phase and 14.6 kcal mol\(^{-1}\) in the solvent. This process leads to the formation of decamethylferrocenium \( \text{DMFc}^+ \) and a hydrogen peroxyl radical. The generation of \( \text{H}_2\text{O}_2 \) from the latter is then expected to proceed rapidly. Note that other possible mechanistic routes occurring via either a superoxoiron \( [\text{DMFc}–\text{O}_2] \) (i.e. protonation last, spin-forbidden) or a superoxide intermediate \( [\text{DMFc}–\text{O}_2\text{H}]^+ \) (i.e. insertion into the Fe–H bond) were found to have considerably higher activation energy barriers than the mechanism proposed above (see details in Supplementary Data). In the case of proton reduction, hydrogen evolution can proceed via a proton attack on \( \text{DMFcH}^+ \) or by a bimolecular route involving two \( \text{DMFcH}^+ \). The present experimental results confirm that hydrogen production is a much slower process than oxygen reduction, which could be explained by the bimolecular pathway.

In conclusion, oxygen/proton reductions by \( \text{DMFc} \) in 1,2-dichloroethane have been observed experimentally. DFT computations suggest a reaction pathway involving protonated \( \text{DMFc} \), \( \text{DMFcH}^+ \), as an intermediate species, which reacts with oxygen to produce hydrogen peroxide. This study shows that protonated metallocenes are highly reactive in reduction reactions useful to energy research such as hydrogen production, oxygen or even carbon dioxide reduction.

This work was supported by EPFL, the Swiss National Science Foundation (FNRS 200020-116588) and the COST Action, D36/007/06. C. C. acknowledges the Sandoz Family Foundation. I. H. also gratefully acknowledges the Scientific and Technological Research Council of Turkey (TUBITAK) under the 2212-PhD Scholarship Programme. Z. S. is also grateful to the Grant Agency of the Czech Republic (grant no. 203/07/1257). We also thank Prof. C. Amatore (ENS, Paris) for helpful discussions.

### Notes and references

HTB was prepared by shaking \( x \) mM LiTB and 10 mM HCl in the water phase with pure DCE for 1 h. The concentration of HTB extracted to DCE was approximately \( x \) mM, as determined by the pH change of the water phase before and after shaking.