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

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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.

O_2 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, O_2 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, O_2 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 H_2O_2.[7] These results suggest the occurrence of oxygen reduction to H_2O_2 by DMFc in DCE in the presence of the organic acid:

$$2DMFc + O_2 + 2H^+TB^- \rightarrow 2DMFc^+TB^- + H_2O_2 \quad (1)$$
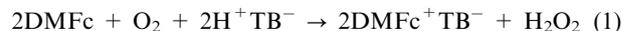
However, only 0.03 mM of H_2O_2 was detected, an amount which is about five times less than that of DMFc$^+$ produced (1.5 mM). This indicates a much lower yield than the stoichiometric value for H_2O_2. One possible reason is the further reduction of H_2O_2 by DMFc to finally produce water. Indeed, in biphasic systems, the yield of H_2O_2 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 H_2 signal can be observed confirming similar results to

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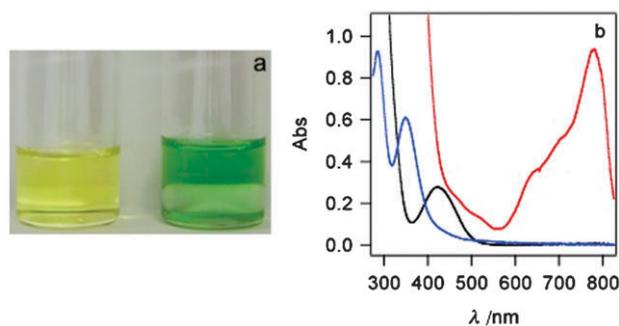
Fig. 1 (a) Colour change of a DCE solution containing 2 mM DMFc before (left) and after (right) addition of 2 mM HTB under aerobic conditions for 30 min; (b) UV-Visible spectra of DCE solutions shown in Fig. 1a (black line: left flask, red line: right flask) and pure water after being shaken with the organic solution in the right flask and addition of sodium iodide (blue line).
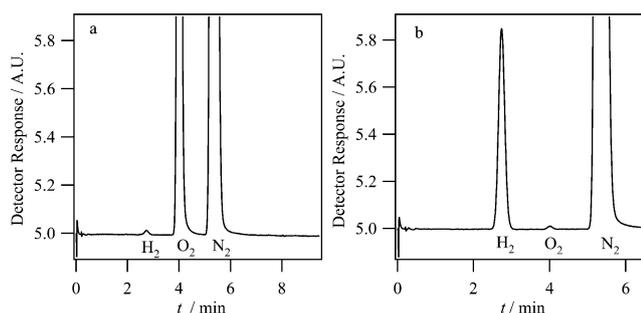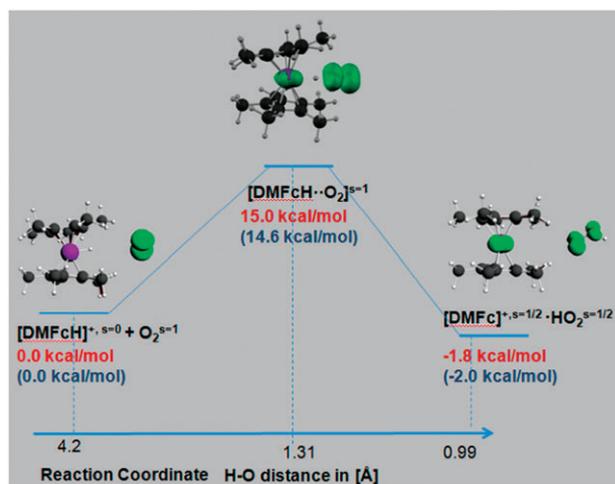
Fig. 2 Gas chromatogram of the head space after 3 h in anaerobic (a) and aerobic conditions (b) for a DCE solution containing 5 mM DMFc and 10 mM HTB.

Scheme 1 Proposed mechanism for the reduction of O_2 into HO_2 by DMFc. Gas phase zero-point corrected energies computed at the BP86/DZP level are given in red. COSMO corrected energies ($\varepsilon = 10.36$) computed at the same level are given in blue. The unpaired spin density is displayed in green. The spin quantum number (*i.e.* s) is given as a superscript for each compound. Further details can be found in the Supplementary Data.†

those obtained in biphasic systems,[9] whereas some small amount of 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 H_2O_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 DMFc leading to the formation of DMFcH$^+$. The protonation of ferrocene was reported to result in a tilting of the rings thus facilitating the binding of O_2 at the Fe atom directly, which is then followed by oxygen reduction.[2] Considering that insertion of triplet O_2 is spin-forbidden, Fomin proposed the formation of an hydrogen-bond intermediate, O_2 being sandwiched between two protonated ferrocenes followed by the generation of H_2O_2 by concerted breakdown of two Fe–H and formation of two H–O bonds.[10] The present DFT computations do not support the hypothesis that triplet molecular oxygen 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 O_2 can approach the activated hydride directly *via* a delocalized triplet (diradical) transition state [DMFc···H···OO]$^+$ (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 DMFc$^+$ and a hydrogen peroxyl radical. The generation of H_2O_2 from the latter is then expected to proceed rapidly. Note that other possible mechanistic routes occurring *via* either a superoxoiron [DMFc–O$_2$] (*i.e.* protonation last, spin-forbidden) or a super-oxide intermediate [DMFc–O$_2$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 DMFcH$^+$ or by a bimolecular route involving two 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 DMFc in 1,2-dichloroethane have been observed experimentally. DFT computations suggest a reaction pathway involving protonated DMFc, 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.

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.

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