Photo-induced biphasic hydrogen evolution: decamethylosmocene as a light driven electron donor

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Abstract

The excitation of the weak electron donor decamethylosmocene on illumination with white light produces an excited state species capable of reducing organic solubilised protons under biphasic conditions. Insights into the mechanism and kinetics of light-driven biphasic hydrogen evolution were obtained by analysis with gas chromatography, cyclic voltammetry, UV/vis and $^1$H NMR spectroscopy. The formation of the decamethylosmocenium hydride, occurring prior to hydrogen evolution, is a rapid step relative to hydrogen release and takes place independently of light activation. Remarkably, hydride formation occurs with a greater efficiency (ca. 90% conversion) under biphasic conditions than when the reaction is carried out in an acidified single organic phase (ca. 20% conversion). Cyclic voltammetry studies reveal that decamethylosmocene has a higher proton affinity than either decamethylferrocene or osmocene.
1. Introduction

Photochemical water splitting or water electrolysis whereby electricity is generated from renewable sources (e.g. solar light or wind) are attractive approaches to produce molecular hydrogen (H₂).[1-5] The “fuel”, water, can provide an almost unlimited source of protons and the only products of the reaction are H₂ and O₂. This article is dedicated to Prof. Adam Heller, who has made influential contributions to the field of solar energy conversion, and will have seen over his long and illustrious career an explosion of productivity and development with regard to the primary focus of this article; light driven hydrogen evolution.[6-7]

The development of novel methodologies to perform the kinetically challenging Hydrogen Evolution Reaction (HER), whereby aqueous protons are reduced to H₂, is of vital technological importance for future solar-based carbon-neutral energy production.[8-12] State-of-the-art multi-component photocatalytic systems combine the use of (a) noble metal-free catalysts based on the first-row transition metals, such as bio-mimetic di-iron[13-14] or cobalt complexes (in particular the cobaloxime series),[15-18] (b) inorganic photosensitizer, either molecular in nature or based on semiconductor particles, and (c) suitable sacrificial electron donors. The bulk of the initial multi-component systems investigated utilized ruthenium photosensitizer in combination with noble-metal free catalysts,[6] which subsequently inspired the use of alternative photoactive complexes based on iridium,[19] rhenium[20] or platinum[21] metal centers, non-noble metal-based photosensitizer (Eosin Y or Rose Bengal),[22-23] and metalloporphyrins.[24-25] Semiconductor based photocatalysts and their composites may also be incorporated into such systems and are often further modified by doping, dye-sensitisation or combination with smaller band-gap semiconductors to enhance their visible light absorption characteristics.[26] Inspired by the light-harvesting complex in photosynthetic
organisms, within which chlorophyll self assembles to build the functional units that carry out the light-harvesting and charge separation processes, an alternative recent approach is to develop supramolecular photocatalysts linking the light-harvesting unit to the catalytic one either by supramolecular assembly (several cobaloxime-photosensitizer complexes have been reported)\textsuperscript{[25, 27]} or via covalent linkages (\textit{e.g.} electronically linking a cobaloxime species and ruthenium sensitizer \textit{via} a TiO\textsubscript{2} nanoparticle).\textsuperscript{[28]} In theory, the optimization of electron transfer in such supramolecular assemblies allows enhanced activity in comparison to a corresponding multicomponent system. Typical electron donor species include ascorbic acid (AA), triethylamine (TEA), triethanolamine (TEOA), tetra-acetic acid (EDTA) or Na\textsubscript{2}S/Na\textsubscript{2}SCN.

All of the systems summarized \textit{vide supra} are generally carried out in a single phase, be that aqueous or organic. However, it has been suggested that the separation of charges, the step that mainly determines the quantum yield in photochemical reactions, should be more efficient when the photoproducts of the reaction are separated in different phases, as in the light-harvesting complex of photosynthetic organisms.\textsuperscript{[29-30]} Besides fulfilling this condition, the \textit{interface} between two immiscible electrolyte solutions (ITIES)\textsuperscript{[31-35]} is recognized as a catalytic platform itself since the separation of the reactants and products in two different phases can shift the equilibrium, thus favoring the thermodynamically desirable reaction.\textsuperscript{[30]} In addition, recently it has been shown that the ITIES also provides a novel platform to develop new multi-component or, indeed, supramolecular (\textit{i.e.} the soft interface may provide a suitable environment for the interfacial self-assembly of an organic solubilised catalyst and aqueous solubilised photosynthesiser or \textit{vice versa})\textsuperscript{[36-37]} catalytic systems, which may potentially be extrapolated to photochemical reactions such as hydrogen evolution.

Polarisation of the ITIES, either chemically (by distribution of electrolyte ions) or potentiostatically, provides an electrochemical driving force facilitating the biphasic HER by
pumping aqueous protons to an organic phase containing a suitable electron donor.\textsuperscript{[38]} Herein, we report an organic soluble sacrificial electron donor, decamethylosmocene (DMOc), that is capable of proton reduction in the absence of a photosensitizer under white light illumination in anaerobic conditions. However, decamethylosmocene remains inactive as an electron donor in the dark, \textit{i.e.} it combines the characteristics of both an electron donor and a sensitizer. Decamethylosmocene is one of a series of related transition metal complexes known as metallocenes, a class of hydrophobic compounds that exhibit highly reversible electrochemistry and are therefore widely used as an “indicator” of potential scale in non-aqueous solvents.\textsuperscript{[39]} Amongst these metallocenes decamethylferrocene (DMFc; redox potential vs. SHE in 1,2-dichloroethane, \textit{E}^0_{\text{DMFc}^-/\text{DMFc}} = 0.04 \text{V})\textsuperscript{[40]} and cobaltocene (Coc; \textit{E}^0_{\text{Coc}^-/\text{Coc}} = –0.69 \text{V})\textsuperscript{[41-42]} are sufficiently strong reducing agents to drive the biphasic HER under anaerobic conditions in the dark. Whereas the rate of the biphasic HER is rapid with cobaltocene, it is rather slow when using decamethylferrocene as an electron donor and needs to be catalyzed by using a variety of noble (Pt, Pd)\textsuperscript{[40]} and non-noble (nanocrystalline MoS$_2$, MoS$_2$ nanoparticles grown on graphene or mesoporous carbon supports, Mo$_2$C, MoB, WC, W$_2$C)\textsuperscript{[43-45]} species. Recently, osmocene (Oc), a much weaker reducing agent (\textit{E}^0_{\text{Oc}^-/\text{Oc}} = 1.03 \text{V}), was found to split water, albeit with a low yield and low quantum efficiency, under anaerobic biphasic conditions on illumination with white light but remained inactive as an electron donor in the dark.\textsuperscript{[46]} Thus, decamethylosmocene, with a reduction potential between that of decamethylferrocene and osmocene (\textit{E}^0_{\text{DMOc}^-/\text{DMOc}} = 0.48 \text{V}), was expected to produce quantitative amounts of H$_2$ upon white light illumination.

2. Results and Discussions
2.1 Photo-induced biphasic HER shake-flask studies.

2.1.1 Preliminary experiments.

The ability of DMOc to successfully act as a light-driven organic electron donor in the biphasic HER was initially investigated by “shake-flask” reactions involving chemical polarization of the interface.\[^{47-48}\] As outlined in Scheme 1(A), an aqueous solution (w) containing 100 mM HCl and 5 mM lithium tetrakis(pentafluorophenyl)borate diethyletherate (LiTB-DEE) was contacted with a 1,2-dichloroethane (1,2-DCE) solution containing 2.5 mM DMOc and 5 mM bis(triphenylphosphoranylidene) ammonium tetrakis-(pentafluorophenyl)borate (BATB) with moderate stirring, under white light illumination and anaerobic conditions. The role of the tetrakis(pentafluorophenyl)borate anion (TB\(^-\)) is to act as a phase transfer catalyst for the extraction of protons to the organic phase (o) as hydrogen tetrakis(pentafluorophenyl)borate diethyletherate (HDEETB, referred to hereafter as HTB for simplicity). Diethylether (DEE) acts as a lipophilic base.

\[
\text{H}^+ \text{,w} + \text{TB}^{-} \text{,w} \rightarrow \text{HTB}^{o} \quad (1)
\]

The initial partition of the individual electrolyte ions in the biphasic system outlined in Scheme 1(A) established an interfacial Galvani distribution potential \((D_{o\text{-w}})\) of 0.504 V for all ions at equilibrium (see Supporting Information for details). This potential was sufficient to extract protons in the form of HTB to 1,2-DCE almost quantitatively with a concentration of 4.97 mM at equilibrium (Table S1, Supporting Information). The transferred protons may subsequently undergo reduction by the light-driven organic electron donor, DMOc, and the reaction in Equation (2) proceeds until the supply of DMOc is exhausted.

\[
\text{DMOc}^{o} + \text{H}^{+o} \xrightarrow{hv} \text{DMOc}^{+o} + \frac{1}{2} \text{H}_2 \quad (2)
\]
The H₂ generated from a shake-flask experiment under white light illumination was analyzed by gas chromatography (GC) after 120 min. An initial comparison was made between the amounts of H₂ evolved in the presence (1.7 µmol) and absence (0 µmol) of white light after 120 min. (Figure 1(A)). The absence of H₂ evolution in the dark confirms that the standard redox potential of the ground state of DMOc in 1,2-DCE \(E^0_{\text{DMOc} - /\text{DMOc} \cdot}^{1,2\text{-DCE}}_{\text{SHE}} = 0.48 \text{ V, see Figure S1, Supporting Information}\) is insufficiently reducing to act as an electron donor for organic solubilised protons, \(E^0_{\text{H}^+/\text{H}_2}^{1,2\text{-DCE}}_{\text{SHE}} = 0.55 \text{ V,}\) as discussed in more detail later, an initial step in the biphasic H₂ evolution mechanism is the rapid formation of the decamethylosmocenium hydride ([DMOc(H⁻)]⁺) on contacting the acidic aqueous phase with the organic phase, which in turn suggests that the following step of hydrogen release is rate limiting. Thus, excitation of DMOc or, indeed, [DMOc(H⁻)]⁺ by white light generates either DMOc⁺ or [DMOc(H⁻)]⁺, respectively. (Note that white light, encompassing the full spectrum of wavelengths, was utilized to ensure the generation all possible excited states, including [DMOc(H⁻)]⁺). Identification of the specific excited state species with the necessary thermodynamic driving force to reduce organic solubilised protons was outside the scope of this article. Further control experiments monitored by GC confirmed that, besides white light, each of the other constituents of the shake-flask experiments were essential to achieve the photo-induced biphasic HER. Shake-flask reactions where either the organic solubilised electron donor (DMOc), the source of protons in the aqueous phase (i.e. carrying out experiments with neat water instead of aqueous HCl) or the polarizing molecule (LiTB-DEE) were removed, failed, in each case, to evolve H₂ (data not shown).

The light-driven biphasic HER was also evaluated by monitoring changes in the UV/vis adsorption spectra for the conversion of organic solubilised DMOc (band centred at 243 nm, no observable absorption bands in visible region) to [DMOc(H⁻)]⁺ (\(\lambda_{\text{max}} = 288 \text{ nm}\))
and DMOc\(^{+}\) (\(\lambda_{\text{max}} = 462\) nm and a smaller broad band centred at 798 nm), see Figure 1(B).

The acquired UV/vis spectra were unambiguously assigned to DMOc\(^{+}\) by comparison with the UV/vis spectra of pure [DMOc\(^{+}\)][BF\(_{4}\)] crystals dissolved in 1,2-DCE (Figure 1(B)).

### 2.1.2. Quantitative determination of shake-flask reaction products and kinetic studies.

The progress of the light-driven biphasic HER was first assessed by monitoring the quantities of H\(_2\) evolved with time for the shake-flask experiments outlined in Scheme 1(A) (\(x = 2.5, y = 5\)) using a calibrated GC, see Figures 2(A) and (B). The maximum quantity of H\(_2\) that may evolve is limited by the initial quantity of DMOc in 1,2-DCE and the duration of white light illumination, varied between 0 and 300 min. The experiments herein are designed with an excess of HTB, however they may be easily re-designed with HTB as the limiting factor, if required, by having a substantially greater [DMOc\(^{\circ}\)] than [LiTB-DEE\(^{+}\)]. The quantities of H\(_2\) evolving with time began to plateau after 180 min. (Figure 2(B)) and the quantity of H\(_2\) evolved after 300 min. (2.1 \(\mu\)mol) corresponded well with the maximum theoretical stoichiometric amount of H\(_2\) (2.5 \(\mu\)mol). The theoretical amount of H\(_2\) evolved was limited (a) by a small quantity dissolved in both phases according to Henry’s equation and (b) the initial [DMOc\(^{\circ}\)] (5 \(\mu\)mol) according to a global HER reaction with the following stoichiometry

\[
\text{DMOc}^{\circ} + \text{H}^+ \xrightarrow{\text{hv}} \text{DMOc}^{+} + \frac{1}{2}\text{H}_2
\]

The progress of the light-driven biphasic HER was also assessed by quantitative determination of the concentrations of DMOc\(^{+}\) in the organic phase using UV/vis spectroscopy. This was feasible by elucidation of the molar extinction coefficient (\(\epsilon, \text{mM}^{-1} \cdot \text{cm}^{-1}\)) of DMOc\(^{+}\) in 1,2-DCE as 0.26 mM\(^{-1} \cdot \text{cm}^{-1}\) for the absorption peak at \(\lambda_{\text{max}} = 462\) nm
(Figure 2(C)). A value of $\varepsilon$ of 0.11 mM$^{-1}$·cm$^{-1}$ was also determined for the broad peak centered at 798 nm but not used for quantitative analysis in our studies.

The ability to quantitatively determine both shake-flask reaction products, $H_2$ and DMOc$^+$, permitted the application of the method of initial rates to determine the kinetics of the HER outlined in Equations (1) and (2) or globally in Equation (3). In the first instance, the initial [LiTB-DEE$^\text{w}$], and hence [HTB$^o$], was maintained constant at 5 mM while the concentration of [DMOc$^o$] was varied between 0 and 5 mM (Figure 3(A)). Next, the initial [DMOc$^o$] was maintained constant at 5 mM while the concentration of [LiTB-DEE$^\text{w}$], and hence [HTB$^o$], was varied between 0 and 5 mM (Figure 3(B)). The reaction in Equation (2) was found to be first order in both [DMOc$^o$] and [HTB$^o$] with a linear dependence in the reaction velocities observed when either [DMOc$^o$] (Figure 3(A)) or [HTB$^o$] (Figure 3(B)) were varied, irrespective of which reaction product was monitored. Thus, the rate of reaction for the light-driven biphasic HER can be written as

$$u = k[DMOc^o][HTB^o]$$

where $k$ is the apparent rate constant for the reaction, calculated as 0.76 M·min$^{-1}$. Also, the rate of DMOc$^+$ formation in the organic phase was approximately twice that of $H_2$ evolution, supporting the stoichiometry outline in Equation (2). An alternative, and equally applicable, way of expressing the rate of reaction would be to consider the global reaction in Equation (3) such that

$$u = k[DMOc^o][LiTB-DEE^w]$$

The apparent quantum yield (AQY), defined by Equation (6), of the light reaction between DMOc and protons was determined to be 0.052 % ($\lambda_{\text{irr}} = 365$ nm, see Supporting Information for calculations).

$$AQY \text{ (\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$ (6)
2.1.3 ¹H NMR studies.

¹H NMR spectroscopy was used as an additional probe to further elucidate the mechanism of the light-driven HER with DMOc. A freshly prepared solution of neutral DMOc in CDCl₃ containing 5 mM BATB, with no exposure to air or white light illumination, exhibited a single peak (δ = 1.72 ppm) indicative of the protons of the methyl groups on both cyclopentadienyl rings,[⁵¹] see Figure S2, Supporting Information. To study the biphasic HER reaction by ¹H NMR spectroscopy, a specially designed shake-flask experiment (shown in Scheme 1(B), x = 5, y = 5), was required where 1,2-DCE was replaced with CDCl₃. On contacting the two phases for 35 min. in the dark under anaerobic conditions a weak signal for unreacted neutral DMOc (δ₁ = 1.75 ppm) and two further signals characteristic of the hydride species [DMOc(H⁻)]⁺ (δ₂ = 1.99 ppm, once more indicative of the protons of the methyl groups on both cyclopentadienyl rings, and δ₃ = −15.62 ppm, indicative of the hydride proton)[⁵²–⁵³] were observed, see Figure S(3), Supporting Information. Under biphasic conditions DMOc was found to be approximately 90% converted to [DMOc(H⁻)]⁺ after 30 min. The hydride species may be formed either by diffusion of organic solubilised DMOc to the interface where it reacts with an aqueous proton,

\[
\text{DMOc}^\circ + \text{H}^{+,\text{aq}} \rightarrow [\text{DMOc(H})^-]\]⁺ \\
(7)
\]

or reaction of DMOc with an organic solubilised proton pumped across the interface under chemical polarisation (Equations (2) and (8)).

\[
\text{DMOc}^\circ + \text{H}^{+,\text{o}} \rightarrow [\text{DMOc(H})^-]\]⁺ \\
(8)
\]

A control experiment illuminating the flask in Scheme 1(B) with white light, again for 30 min. under anaerobic conditions, was performed and an identical ¹H NMR spectrum was detected showing approximately 90% conversion of DMOc to [DMOc(H⁻)]⁺ in the organic phase, see Figure S4, Supporting Information. These observations indicate that (a) hydride
formation is independent of white light illumination and (b) the protonation step under biphasic conditions is relatively fast, especially considering that completion of the global biphasic HER (Equation (3)) under white light illumination requires up to 300 min. (see Figures 2 (A) and (B)). A previous report has shown that DMOc may undergo UV photolysis under certain experimental conditions to form mono- or di-cations on losing protons from the cyclopentadienyl rings.\[53\] Herein, however, under the biphasic experimental conditions outlined in Scheme 1(B), no such signals were observed in the $^1$H NMR spectra upon white light illumination indicating the absence of any such side-reactions.

Subsequently, a comparative study was undertaken to study hydride formation in a single phase. DMOc was dissolved in an organic phase (CDCl$_3$) containing both HTB and BATB, prepared as described previously.\[54\] In such a scenario hydride formation can only take place by association of DMOc with organic protons. Interestingly, in the dark, protonation in a single phase proceeded much slower than was the case for a biphasic system, under otherwise identical experimental conditions. After 80 hrs. approximately 20% conversion to the hydride took place, perhaps indicating a weaker acid dissociation constant in the organic phase, see Figure 4 for a time-course of the hydride formation. Additionally, under white light illumination, on close inspection of the resultant $^1$H NMR spectrum a broad and weak peak ($\delta = 22$ ppm) was observed in the low field of the spectrum and suggested to be DMOc$^{**}$,\[55\] see Figure S5, Supporting Information.

2.2 Voltammetry studies at the liquid|liquid interface.

Thus far, the thermodynamic driving force pumping protons into the organic phase and enabling the biphasic HER reaction, see Equation (3), to occur has been provided by chemical distribution of common ions. Potentiostatically polarising the interface in a 4-electrode configuration (see Scheme 2 for the electrochemical cell configuration) may allow
further insights into the mechanistic details of biphasic HER with DMOc. Figure 5(A) shows cyclic voltammograms (CVs), obtained in the dark under anaerobic conditions, comparing the baseline response of the background electrolytes (no electron donor present) at pH 3 with those when 5 mM DMOc was added to the organic phase over the pH range 1 to 3. The potential window of the baseline response was limited by reversible proton and Cl⁻ transfer at the positive and negative limits, respectively. In the presence of DMOc, at each pH value, a large irreversible positive current wave dominates at positive potentials. Considering that organic solubilised DMOc requires photo-activation to act as an electron donor and taking into account that (a) the CVs were recorded in the dark, (b) no hydrogen bubble formation was seen at the ITIES and (c) ¹H NMR studies have shown earlier that [DMOc(H⁻)]⁺ formation is independent of light activation, we may surmise that the only reaction taking place in the dark in the electrochemical cell is the equilibrium between protonation and de-protonation of DMOc, i.e. hydride formation either by aqueous or organic protons. Thus, the forward going (i.e. from negative to positive potentials) current waves in Figure 5(A) may be attributed to the formation of [DMOc(H⁻)]⁺, with DMOc assisting the ion transfer of the proton across the interface. Meanwhile, the absence of any observable return peaks indicates that no dissociation of the hydride species takes place when the sweep is reversed.

The Nernst equation for an assisted ion transfer at the liquid|liquid interface reads \(^{[38]}\)

\[
\frac{w}{o} \frac{\nu}{[\text{DMOc}(\text{H}^-)]^+} = \frac{w}{o} \frac{\nu}{\text{H}^-} + \frac{RT}{2F} \ln \left( \frac{D_{\text{DMOc}}}{D_{[\text{DMOc}(\text{H}^-)]^+}} \right) + \frac{2.303RT}{F} \left( pK_{1,2-\text{DCE}}^{1,2-\text{DCE}} + \frac{2.303RT}{F} p\text{H}^w \right) \quad (9)
\]

where \(w/o \frac{\nu}{[\text{DMOc}(\text{H}^-)]^+}\) is the experimentally observed half-wave potential of the facilitated proton transfer and \(w/o \frac{\nu}{\text{H}^-}\) is the formal transfer potential of a proton (0.55 V vs. SHE).\(^{[49]}\)

\(D_{\text{DMOc}}\) and \(D_{[\text{DMOc}(\text{H}^-)]^+}\) represent the diffusion coefficients of DMOc and [DMOc(H⁻)]⁺ in 1,2-DCE, respectively, and are assumed for simplicity to be equal. Finally, \(p\text{H}^w\) is the pH of the
aqueous phase and $pK_{a,[DMOc(H^-)]^+}^{1,2-DCE}$ refers to the $pK_a$ of [DMOc(H^-)]$^+$ in 1,2-DCE. Equation (9) predicts the pH dependence of the onset potential of the irreversible wave for hydride formation, which was corroborated by the shift of the current signal by $\sim$65 mV pH$^{-1}$ as shown in Figure 5(C). Also, the $pK_a$ of [DMOc(H^-)]$^+$ was estimated using Equation (9) from the intercept of the plot in Figure 5(C), and found to be 8.35. For comparison, previously we have determined the $pK_a$'s of [DMFc(H^-)]$^+$ and [Oc(H^-)]$^+$ to be 6.58 and 6.5, respectively, using an identical analysis.$^{[38, 46]}$ This means that DMOc has a higher proton affinity than either DMFc or Oc ($K_{a,[DMOc(H^-)]^+}^{1,2-DCE} = 4.46 \times 10^{-9}$, $K_{a,[DMFc(H^-)]^+}^{1,2-DCE} = 2.63 \times 10^{-7}$ and $K_{a,[Oc(H^-)]^+}^{1,2-DCE} = 3.16 \times 10^{-7}$).

Comparison of the CVs obtained in Figure 5(A) with those measured previously under identical experiments conditions (in the dark, under a nitrogen atmosphere, etc.) but replacing DMOc with DMFc$^{[38]}$ or Oc$^{[46]}$ in Scheme 2 re-enforce the notion that DMOc is a stronger Brønsted base than either DMFc or Oc. Firstly, the higher proton affinity of DMOc means that [DMOc(H^-)]$^+$ remains undissociated on the reverse sweep thereby producing an irreversible wave. In contrast, [Oc(H^-)]$^+$ dissociates on the reverse sweep resulting in the observation of a reverse peak for the back transfer of protons from the organic to the aqueous phase. Secondly, the current density observed for DMOc is up to 5 times larger than that for an equivalent concentration of DMFc in the organic phase within the same potential window range. This may be due in part to the onset potential for the assisted proton transfer by DMOc, $v_{onset}$, being more negative than that for DMFc at equivalent pHs, as indicated by Equation (9), since the $pK_{a,[DMOc(H^-)]}$, $pK_{a,[Oc(H^-)]}$ and $pK_{a,[DMFc(H^-)]}$, However, despite the trend in $pK_a$ values the current densities for DMOc and Oc are broadly similar. This reflects the fact that hydride formation (and hence the resultant current density
observed) is also dependent on a host of other variables such as, for example, the solubility of the hydride species in the respective phases. A Tafel analysis of the forward going (i.e. from negative to positive potentials) current waves in Figure 5(A) was attempted and is presented in the Supporting Information as Figure S6.

A scan rate study was performed by using the electrochemical cell described in Scheme 2, with DMOc at pH = 1 (Figure 5(B)). The current of the irreversible wave remained independent of the applied scan rate (between 20 and 100 mV·s⁻¹) and the only difference between CVs was the slightly larger capacitance at higher scan rates. Such an observation indicates that, on the timescale of the electrochemical response, the rates of diffusion of protons and DMOc to the interface are faster than their depletion at the ITIES, i.e. the rate of protonation of DMOc to form the hydride species and its diffusion away from the interface.

2.3 Further mechanistic discussion.

At this point it is worth noting that it is not possible to explicitly state the locus of the reaction and distinguish a heterogeneous reaction from a strictly homogeneous one under our experimental conditions. Alternative scenarios include (a) an interfacial reaction upon polarisation of the interface between organic solubilised DMOc and aqueous protons, see Equation (3), or (b) electron transfer between aqueous solubilised DMOc (even if DMOc is sparingly aqueous soluble) and aqueous protons, see Equations (10) and (11).

\[
\text{DMOc}^\circ \rightarrow \text{DMOc}^\wedge \quad (10)
\]

\[
\text{DMOc}^\wedge + \text{H}^\wedge + \text{TB}^\wedge \xrightarrow{hv} \text{DMOc}^{*\circ} + \text{TB} + \frac{1}{2}\text{H}_2 \quad (11)
\]

Irrespective of whether the mechanism proceeds via Equations (2), (3) or (11) (or, indeed, if processes take place simultaneously), the driving force for the reaction is the same, as shown
previously for the case of DMFc,\cite{43} and the net result is the conversion of DMOc to DMOc^{++} and the consumption of protons resulting in the evolution of H_2.

3. Conclusions

These studies identify decamethylosmocene (DMOc) as a sacrificial organic electron donor that upon irradiation, but, notably, in the absence of a dedicated photosensitizer, is capable of reducing organic solubilized protons (either pumped across the interface of a biphasic system due to the presence of a phase transfer catalyst or present initially as an organic acid, \textit{i.e.} HTB, in a single phase), resulting in the production of hydrogen and decamethylosmocenium radical cations (DMOc^{++}). The redox potential of the excited state of either neutral DMOc or the hydride species, [DMOc(H\textsuperscript{−})]^{+}, is sufficiently negative to allow complete consumption of the sacrificial electron donor or organic acid (depending on which is limiting) and, thus, produce the associated quantity of hydrogen after 300 min. \textsuperscript{1}H NMR studies revealed that conversion of DMOc to the hydride species, a key initial step leading to hydrogen evolution, occurs independently of light activation and, interestingly, with a greater efficiency under biphasic conditions than in an acidified single organic phase. The apparent quantum efficiency of the reaction (\(\phi = 0.052\%\) at \(\lambda_{\text{irr.}} = 365\) nm), while still indicating a relatively low yield for the photo-production of hydrogen, nevertheless doubled in comparison to that previously reported for a similar study where osmocene was implemented as the sacrificial electron donor of choice.\cite{46} This work opens new perspectives as the production of hydrogen using light activated weak electron donors is advantageous in so far as relatively weak electron acceptors (generated from a second half-reaction, for example the light driven oxygen evolution reaction) would be required to regenerate both donor and acceptor species, thereby “re-setting” the photo-system.
Experimental Section

Chemicals

All chemicals were used as received without further purification with the exception of decamethylferrocene (DMFc, ≥99%, Alfa Aesar) which was purified by vacuum sublimation at 140 °C before use. All aqueous solutions were prepared with ultra pure water (Millipore Milli-Q, specific resistivity 18.2 MΩ·cm). The solvents used were 1,2-dichloroethane (1,2-DCE, ≥99.8%, Fluka), deuterated chloroform (CDCl3, 99.8+ atom % D, Merck), acetonitrile (CH3CN, ≥99%, Aldrich), diethylether (DEE, ≥99%, Aldrich), acetone (≥99%, Fluka), methanol (≥99%, Fluka), hydrochloric acid (HCl, 37%, Merck) and sulphuric acid (H2SO4, 98%, Merck). Decamethylosmocene (DMOc, 99%) and ferrocene (Fc, 98%) were supplied by ABCR and Aldrich, respectively, and stored under a nitrogen atmosphere until use. Lithium chloride anhydrous (LiCl, ≥99%), anhydrous sodium sulphate (Na2SO4, ≥99%) and tetraethylammonium chloride (TEACl, ≥98%) were ordered from Fluka and silver tetrafluoroborate (AgBF4, ≥99%) from Aldrich.

Lithium tetrakis(pentafluorophenyl)borate diethyletherate (LiTB-DEE, Boulder Scientific) and bis(triphenylphosphorylidene) ammonium chloride (BACl, ≥98%, Aldrich) were used to prepare bis(triphenylphosphorylidene) ammonium tetrakis(pentafluorophenyl)borate (BATB) by metathesis of equimolar solutions of BACl and LiTB-DEE in a methanol/water (2:1 v/v) mixture. The resulting precipitates were filtered, washed and recrystallized from acetone. The decamethylosmocenium tetrafluoroborate ([DMOc“+”][BF4“-”]) was synthesised as O’Hare et al. First, a solution of DMOc (100 mg, 0.21 mmol) dissolved in 1,2-DCE was added dropwise to a solution of AgBF4 (40 mg, 0.20 mmol) prepared in 5 mL CH3CN. Immediately a grey precipitate and green solution were formed. The solution was filtered and then the solvent was removed under reduced pressure.
The resulting orange solid was washed with DEE (2 × 20 mL aliquots) and re-dissolved in 1,2-DCE (10 mL).

**Shake Flask Experiments**

All shake flask experiments, whether characterised by gas chromatography, UV/vis spectroscopy or $^1$H NMR analysis, were prepared using aqueous and organic solutions thoroughly de-gassed with nitrogen, under anaerobic conditions in a glove box purged with nitrogen, either in the dark or under white light illumination, and at an ambient temperature of 23 ± 2 °C. Anaerobic conditions were necessary to avoid competing side-reactions of DMOc with oxygen, such as H$_2$O$_2$ generation, as previously demonstrated by shake flask experiments performed in the dark where DMFc was the organic electron donor of choice.$^{[48, 54, 58-60]}

Two-phase reactions were performed in a septum sealed glass vial. 2 mL of an acidic aqueous phase containing LiTB-DEE was contacted with an equal volume of 1,2-DCE containing the lipophilic electron donor DMOc. Magnetic stirring (900 rpm) was used to emulsify the two phases for the duration of each experiment and the cell was illuminated by white light throughout using a Xenon lamp. The liquid|liquid interface was polarized chemically by distribution of a common ion (highly hydrophobic TB$^-$, initially present in the aqueous phase) across the interface. The expected reaction products from the shake flask, the precise composition of which is outlined in Scheme 1(A), were H$_2$ and the DMOc$^+$, see Equation (2). The presence of both was determined post-shake flask reaction.

*Analysis of H$_2$ evolved.* 1 mL samples of the headspace gas were obtained using a lock-in syringe with a push-pull valve (SGE Analytical Sciences) in a glovebox and subsequently analysed by gas chromatography (GC) using a Perkin-Elmer GC (Clarus 400, equipped with 5 Å molecular sieves and an 80/100 mesh) with a thermal conductivity detector (TCD) and argon as a carrier gas.
Analysis of DMOc** formation by UV/vis spectroscopy. Post-shake flask reaction, the mechanically emulsified phases were first allowed to settle and then the two phases were carefully separated using a glass pipette. UV/vis spectra of ~1.5 mL samples of the organic phase were measured in a glovebox on an Ocean Optics CHEM2000 spectrophotometer using a quartz cuvette with a path length of 1 cm, volume of 4 mL, and equipped with a Teflon cap to prevent evaporation of the organic phase during the analysis. The obtained UV/vis spectra were unambiguously assigned to DMOc** by comparison with the UV/vis spectra of pure [DMOc**][BF_4^-] salts dissolved in 1,2-DCE. Quantitative determination of the concentrations of organic solubilized DMOc** by UV/vis spectroscopy was possible by elucidation of the molar extinction coefficient (ε, mM^-1·cm^-1) of DMOc** in 1,2-DCE. This was calculated from the slope of a plot of absorbance (arbitrary unit) versus [DMOc**] (mM) in a cuvette with a path length of 1 cm. Each point on the calibration plot was prepared by dissolution of [DMOc**][BF_4^-] salts in 1,2-DCE to ensure maximum accuracy and not using the DMOc** product of the biphasic reaction due to the possible presence of unreacted DMOc post-biphasic reaction.

The apparent quantum yield (ϕ) was determined by illuminating a circular area of a shake flask using a mounted high-power light emitting diode (LED) from ThorLabs at λ_{irr} = 365 nm for a specific period of time and the quantity of H_2 evolved was determined by GC.

^1H NMR analysis. The composition of the shake flask analysed by ^1H NMR is outlined in Scheme 1(B). The typical organic phase utilized thus far, 1,2-DCE, was replaced by CDCl_3. BATB (δ_1 = 7.45 ppm, δ_2 = 7.64 ppm) was used as an internal standard. Once more, post-shake flask reaction, the mechanically emulsified phases were first allowed to settle and then the two phases were carefully separated using a glass pipette. ^1H NMR analysis was performed in a NMR tube using a Bruker Biospin Avance-400. Chemical shifts were expressed in ppm relative to chloroform (δ = 7.28 ppm). The presence of water (δ =
1.62 ppm)\textsuperscript{[61]} was confirmed by observation of a significant decrease in this signal’s intensity on addition of anhydrous Na\textsubscript{2}SO\textsubscript{4}. Two signals (δ\textsubscript{1} = 1.25 ppm, δ\textsubscript{2} = 1.50 ppm) were attributed to DEE,\textsuperscript{[61]} extracted to the organic phase on contacting the organic phase with the acidic aqueous phase containing LiTB-DEE.

**Kinetic studies.** The composition of the shake flasks used for kinetics studies is that given in Scheme 1(A). Experiments were performed where the initial concentration of DMOc in 1,2-DCE was varied in the presence of 5 mM organic protons (*i.e.* 5 mM LiTB-DEE was dissolved in the aqueous phase resulting in the transfer of ~5 mM protons to the organic phase in the form of HTB) and the initial concentration of LiTB-DEE in the aqueous phase (thus, in effect, the initial concentration of organic solubilised protons) was varied in the presence of 5 mM DMOc in the organic phase. For each particular concentration of [DMOc\textsuperscript{\circ}], *e.g.* 2.5 mM, while [LiTB-DEE\textsuperscript{w}] was maintained constant at 5 mM, a series of individual shake flasks were prepared and each was illuminated for a different time. Hydrogen evolved or DMOc\textsuperscript{2+} generated from each flask of different reaction were analyzed quantitatively by GC and UV/vis spectroscopy, respectively, whereby a time course curve with respect to either hydrogen or DMOc\textsuperscript{2+} was attained by plotting the amount of hydrogen or DMOc\textsuperscript{2+} against the reaction time. The initial rate was then calculated from the initial three points of the time course curve. The same procedures as mentioned above was repeated except for [LiTB-DEE\textsuperscript{w}] was varied, while [DMOc\textsuperscript{\circ}] was maintained at 5 mM to obtain the initial rates.

**Electrochemical Measurements at the Liquid|Liquid Interface**

Ion-transfer voltammetry experiments at the water|1,2-DCE interface were performed in a four-electrode configuration using a PGSTAT 30 potentiostat (Metrohm, CH). Two platinum counter electrodes were positioned in the aqueous and organic phases, respectively, to supply
the current flow. An external potential was applied by means of silver/silver chloride (Ag/AgCl) reference electrodes which were connected to the aqueous and organic phases, respectively, via a Luggin capillary as illustrated previously.[43] The Galvani potential difference across the interface (\( \Delta \text{w} \)) was estimated by taking the formal ion transfer potential of tetraethylammonium cation (TEA\(^+\)) as 0.019 V.[62] The obtained voltammetry was \( iR \) compensated by using positive feedback to compensate the resistance of the cell. The area of the liquid|liquid interface was 1.53 cm\(^2\). The generic composition of the four-electrode cells studied is given in Scheme 2. All voltammetry experiments were completed using aqueous and organic phases thoroughly de-gassed with nitrogen, under anaerobic conditions in a glovebox filled with nitrogen, in the dark and at an ambient temperature of 23 ± 2 °C.

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Keywords
Decamethylosmocene, hydrogen evolution reaction, liquid|liquid interface, electron donor, biphasic electrochemistry

References

Scheme 1. Photo-driven biphasic hydrogen evolution under chemical polarisation: schematic representation of the initial compositions of the aqueous and organic phases for shake-flask experiments (A) where the products of the biphasic reaction, hydrogen gas and organic solubilised DMOc•+, were monitored by gas chromatography and UV/vis spectroscopy, respectively, and (B) where the organic phase was additionally probed by $^1$H NMR spectroscopy.
Scheme 2. Schematic representation of the composition of the electrochemical cell used for ion transfer voltammetry.
Figures

Figure 1. (A) Gas chromatograms of the shake-flask headspace for two-phase reactions (see Scheme 1(A), x = 2.5, y = 5) after 120 min., under anaerobic conditions, in the dark (solid line) and under white light illumination (dashed line). (B) Comparison of the UV/vis spectra of the organic phase for two-phase reactions (see Scheme 1(A), x = 2.5, y = 5) before (solid line) and after (dashed line) 120 min. of white light illumination, under anaerobic conditions, with a solution of 1,2-DCE containing 2.5 mM of synthesised DMOc\(^+\) (dotted line).
Figure 2. Quantitatively monitoring the products of the biphasic reaction, hydrogen gas and organic solubilised DMOc\textsuperscript{+}. (A) Gas chromatograms of the shake-flask headspace for two-phase reactions (see Scheme 1(A), x = 2.5, y = 5), under anaerobic conditions, as a function of time and (B) the resulting time-course for hydrogen evolution. (C) Elucidation of the molar extinction coefficient ($\varepsilon$, mM\textsuperscript{-1}\cdot cm\textsuperscript{-1}) of DMOc\textsuperscript{+} in 1,2-DCE by plotting the absorbance (arbitrary unit) versus [DMOc\textsuperscript{+}] (mM) (inset) of the UV/vis spectra of 1, 2.5 and 5 mM synthesized DMOc\textsuperscript{+} dissolved in 1,2-DCE.
Figure 3. Kinetics of the photo-driven biphasic hydrogen evolution reaction (HER) with chemically controlled polarisation under white light illumination; method of initial rates. The initial rate (mM min\(^{-1}\)) after 60 min. of illumination with white light was monitored both by gas chromatography (dashed line), to detect evolved H\(_2\), and UV/vis spectroscopy (full line), to detect DMOc\(^{+}\) formation, where (A) the initial [DMOc] in 1,2-DCE was varied in the presence of 5 mM HTB and (B) the initial [HTB] was varied in the presence of 5 mM DMOc in the organic phase.
Figure 4. Time course of hydride $[\text{DMOc}(\text{H}^-)]^+$ formation in a one-phase system containing 5 mM DMOc and 5 mM HTB in CDCl$_3$, monitoring by $^1$H NMR.
Figure 5. Ion transfer voltammetry experiments, see electrochemical cell outlined in Scheme 2. (A) Influence of pH: Cyclic voltammetry (CV) in the absence ($x = 0$) and presence of DMOc ($x = 5$) in the organic phase. The acidity of the aqueous phase was varied from pH 1 to 3 as indicated. CVs were obtained under anaerobic conditions at a scan rate of 20 mV s$^{-1}$. (B) Scan rate study: CVs obtained in the presence of DMOc ($x = 5$) at pH 1. (C) pH dependence of $\Delta_{w}^{\phi}$.