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**Retracted article:** Electrochemical hydrogen production in aqueous micellar solution by a diiron benzenedithiolate complex relevant to [FeFe] hydrogenases

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We, the named authors, hereby wholly retract this Physical Chemistry Chemical Physics article.

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Electrochemical hydrogen production in aqueous micellar solution by a diiron benzenedithiolate complex relevant to [FeFe] hydrogenases†

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The diiron hydrogenase model Fe₂(bdt)(CO)₆ (I, bdt = benzenedithiolate) was dispersed in aqueous micellar solution prepared from sodium dodecyl sulfate (SDS). Aqueous solution of I showed no sign of decomposition when left in contact with air over a period of several days. Current–potential responses recorded at a dropping mercury electrode over pH 7–3 were consistent with reduction of freely diffusing species. Catalysis of proton reduction was observed at pH 6 with current densities exceeding 0.5 mA cm⁻² at an acid-to-catalyst ratio of 17. Bulk electrolysis at −0.66 V vs. SHE of solution of I at pH 3 confirmed the production of hydrogen with a Faradaic efficiency close to 100%. A mechanism involving initial reduction of I and subsequent proton-coupled electron transfer is proposed.

1. Introduction

A basic limitation to large-scale production of molecular hydrogen (H₂) by photochemical and electrochemical water splitting is the lack of catalysts based on cheap and abundant material.¹–⁵ Catalysis of proton reduction by cobalt and nickel compounds has been extensively studied.⁶–⁸ However, the natural abundance of these two transition metals is rather low (20 ppm and 90 ppm, respectively) as compared to iron (6.3%). Inspiration for the design of iron-based catalysts might be provided by the FeFe-hydrogenases ([FeFe]-H₂ases), a class of enzymes catalyzing the production of H₂ at high rates.⁹,¹⁰ Indeed the active site of these enzymes contains a Fe₂S₂ core that has inspired, over the last decade, the synthesis of numerous structural and functional models of the type Fe₂(SR)₂(CO)₆ (Scheme 1).¹¹–¹⁴ While the use of water as a proton source for H₂ production is highly desirable, the lack of solubility of the majority of the [FeFe]-H₂ase models in aqueous media limited their study to organic solvents.¹⁵ In an attempt to solve this issue, polymers functionalized with a diiron model complex were grafted on electrodes, but they showed poor catalytic activity.¹⁶ On the other hand, few diiron models holding hydrophilic ligands were prepared, which permitted us to confirm the stability and activity of this type of catalyst in mixtures of organic solvent and water.¹⁷–¹⁹ A recent report from Darensbourg and co-workers described the synthesis of sulfonated diiron derivatives that could be included in β-cyclodextrin.²⁰,²¹ This approach solves the problem of water solubility and offers moreover the possibility of mimicking the protein environment of the H₂ases. Unfortunately, addition of β-cyclodextrin tends to hinder the electrochemical activation of proton reduction by the diiron catalyst on a glassy carbon electrode. A few studies concerning photodriven H₂ production by diiron models in aqueous solution containing or not a fraction of organic solvents were also recently reported.²²,²³ In particular, Wu and coworkers showed that water-insoluble diiron models and photosensitizers could be incorporated into micelles formed in an aqueous sodium dodecyl sulfate (SDS) solution.²⁴ This system produces H₂ with low rates using ascorbic acid as a sacrificial electron donor. However, the catalytic properties of the diiron models were not independently evaluated in aqueous SDS solution. Whether the H₂ production rate is limited by the activity of the catalyst, the coupling with the photosensitizer, or any other step was therefore not established. While micelles formed by surfactants in water are simple models of biological membranes, much of their interest relates to the possibility of dispersing a water-insoluble substance into a medium that is overall an aqueous one.²⁵ In particular, electrochemical data for a variety of organic molecules and transition
metal complexes in an aqueous electrolyte could be obtained by dispersion in micelles. Electrochemical studies of water-insoluble substances moreover showed that micelle systems are able to stabilize reactive intermediates in aqueous solution.

In view of these previous results, we focused on electrochemistry of the water-insoluble diiron model Fe₉(bdt)(CO)₆ (I, bdt = benzenedithiol, Scheme 1) dispersed in aqueous SDS solutions. Compound I was chosen because it is an air-stable binuclear iron(i) species.²⁶ Besides, it holds a bdt-bridging ligand that helps maintaining the integrity of the Fe₂S₂ core in the reduced iron(0) states.²⁷ Previous works from our laboratory showed that I is actually a robust but qnot very active catalyst for the reduction at mild potential of organic acid in non-aqueous solvents.²⁸²⁹ Herein, we demonstrate that I in aqueous SDS solutions is in contrast an active H₂ production catalyst operating at potentials positive to −0.7 V vs. SHE at pH ≈ 3.

2. Experimental

Fe₉(bdt)(CO)₆ (I) was prepared in moderate yield from reaction of Fe₉(CO)₁₂ with 1,2-benzenedithiol by slight modification of previously reported procedures.³⁰ Analytical grade chemicals and Milli-Q water were used in the preparation of aqueous solutions. To prepare aqueous solution of I, it was more convenient to dissolve the compound in a little methanol and then to dilute the resulting solution in water. In our experiments, the final concentration of methanol in water was lower than 0.25% v/v and had no detectable effect upon the results. Addition of SDS above the critical micellar concentration (10 mM) was however required to obtain aqueous solutions of I that did not look clouded at concentrations relevant to catalysis. Absorption spectra were recorded in quartz cells in contact with air on a Jasco V-670 Spectrophotometer. Current–potential responses of N₂-purged solutions of I were recorded unless otherwise noted on a dropping mercury electrode of 0.0052 cm² using a Metrohm VA 663 Stand. The reference electrode was a commercial Ag/AgCl, 3 M KCl electrode and the potentials are reported with respect to SHE by adding 0.208 V to the experimentally obtained values. Bulk electrolysis of 10 mL of solution of I was carried out at controlled potential on a stirred mercury pool of about 7 cm², while the Pt counter electrode was separated from the working electrode compartment by a fine porosity glass frit of about 0.2 cm². Faradaic efficiency was determined by pH increase measured with a glass electrode connected to an Orion Research pH/millivolt-meter model 811. The presence of H₂ in the electrolysis cell headspace was confirmed by analysis on a Varian 3900 Gas Chromatograph equipped with a TCD and a Porapak Q80/100 column (2 m × 1/8 in) using N₂ as a vector gas.

3. Results and discussion

3.1. UV-visible spectra of aqueous solution of I

The absorbance spectrum of I in phosphate buffer solution at neutral pH shows an intense peak at 346 nm (ε = 7230 M⁻¹ cm⁻¹) and a broad shoulder at 485 nm (Fig. 1). These features are similar to those of comparable diiron dithiolate complexes.³¹ Addition of SDS gradually shifts the absorption bands towards the UV region. Once the critical micellar concentration is reached the absorption spectra become independent of SDS concentration ([SDS] ≥ 10 mM, λmax = 335 nm, ε = 9530 M⁻¹ cm⁻¹), suggesting an interaction of I with the micelles. Absorbance at λmax obeys Beer’s law for [I] ≤ 0.2 mM showing that the diiron compound is well dispersed in SDS aqueous solution at concentrations relevant to catalysis (Fig. S1, ESI†). Decreasing the pH of the solution has no noticeable influence on the absorption spectra, indicating that I does not react with protons at pH > 3 (Table S1, ESI†).³² Interestingly, compound I shows no visible sign of degradation in solutions left in contact with air over a period of several days, as confirmed by UV-visible spectroscopy and electrochemistry.

3.2. Polarography of aqueous solutions of I

Compound I exhibits a chemically reversible two-electron reduction in organic solvents. The reduced species I²⁻ reacts with strong organic acid (pKᵣ < 20) to catalytically produce H₂.²⁸²⁹ As we wanted to know whether a similar mechanism could occur in water, electrochemistry of aqueous SDS solutions of I was investigated at neutral and acid pH. Additionally, current–potential curves were recorded at a dropping mercury electrode to avoid strong adsorption of I and SDS observed with the glassy carbon electrode (Fig. S2, ESI†). Polarograms of I at neutral pH show a primary reduction step at E1/2 = −0.74 V (half-wave potential; all potentials are referenced to SHE, Fig. 2), a potential consistent with the mild reduction of the bdt-diiron derivatives in organic solvent.²⁸²⁹ We also note that this potential value is about 0.6 V less negative than those reported for the reduction in water of diiron models bearing hydrophilic ligands.¹⁷¹⁹ Linear dependence of the cathodic current on [I] moreover indicates the reduction of a free-diffusing species, confirming that there is no adsorption on the electrode. Primary reduction of I is followed by a second reduction event at about −0.90 V preceding a sharp rise in current at −1.05 V, suggesting catalytic reduction of water by a reduced form of I (vide infra). In organic solvents, compound I is reduced to its dianion in a chemically reversible two-electron process.

Fig. 1 UV-visible absorption spectra of 32 μM Fe₉(bdt)(CO)₆ (I) in 0.1 M phosphate buffer solution at pH 6.8 before (black trace) and after (red trace) addition of 10 mM SDS.
However, the number of electrons involved in the reduction of I at neutral pH cannot be estimated from the polarograms presented here because we suspect that the reduction of I is coupled to a protonation step.

Polarograms of I recorded in the presence of 10 mM acetic acid (HOAc) show a sharp current increase at a potential slightly less negative than that of the primary reduction of I at neutral pH (Fig. 3). The reduction of acid on the mercury electrode occurs at potentials more negative than −1.2 V. The current increase is therefore due to catalytic reduction of acid mediated by I. From the peak current value, we calculated a current density exceeding 0.5 mA cm\(^{-2}\) for \([I] = 60\ \text{µM}\) and \([\text{acid}] / [I] = 17\). Additionally, the catalytic current depends linearly on \([I]\) demonstrating that homogeneous catalysis does occur.

Control experiments were carried out to confirm the catalytic activity of I. Polarograms of Fe(SO\(_4\)) in SDS solution at neutral pH show that the reduction of Fe\(^{2+}\) occurs at potentials more negative than that of I. The cathodic current is moreover poorly responsive to pH (Fig. S3, ESI\(^+\)), indicating that the low valence iron species formed upon reduction of Fe\(^{2+}\) are not able to catalyse proton reduction.

A plot of the ratio of the catalytic current \((i_c)\) to the current for the reduction of I at neutral pH \((i_p)\) versus the acid concentration is shown in Fig. 4. Addition of acetic acid results in a substantial current enhancement that depends linearly on \([\text{HOAc}]^{1/2}\), suggesting that reaction is first order in acid as seen in organic solvents.\(^{29}\) At higher acid concentration, the current enhancement levels off, eventually reaching a maximum \(i_c/i_p = 80\) at acid concentrations above 5 mM (the acid-independent region). It is noteworthy that a significantly lower current enhancement \((i_c/i_p < 3)\) was measured in acetonitrile in the presence of a large excess of toluenesulfonic acid as a proton source (Table S3, ESI\(^+\)).

Dubois and co-workers\(^{33}\) proposed a method for evaluating the turnover frequency (TOF) of a catalyst from the maximum of current enhancement in the acid-independent region. Unfortunately, this method implies measurements at increasing scan rates, which cannot be done at a dropping mercury electrode. Voltammetry at a dropping mercury electrode showed that the maximum of current enhancement becomes independent of the scan rate above 50 mV s\(^{-1}\) (Fig. S4, ESI\(^+\)). The value \(i_c/i_p \approx 120\) measured at \(\nu = 100\ \text{mV s}^{-1}\) is in good agreement with the slightly lower value of 80 measured at 2.5 mV s\(^{-1}\) with a dropping mercury electrode under otherwise similar conditions ([I] = 20 µM, [HOAc] = 10 mM, Fig. 4). According to Dubois, the catalytic current enhancement \((i_c/i_p)\) is related to the catalyst turnover frequency by: TOF = 1.93 × \(\nu \times (i_c/i_p)\).\(^{3}\) The value calculated here, TOF \(\approx 2600\ \text{s}^{-1}\), is several orders of magnitude larger than that measured in organic solvents. This is however a rough estimation because first there is a strong indication that the current \(i_p\) measured at neutral pH actually corresponds to the current for the reduction of I coupled with a protonation step and second the catalytic waves are rather peak shaped than S-shaped as would be expected from the theory. Note however that our electrochemical measurements are consistent with the high rate of photochemical hydrogen production previously obtained with a bdt diiron derivative in a 1:1 DMF/water mixture.\(^{22}\)

### 3.3. Bulk electrolysis of acid solutions of I

To confirm the catalytic efficiency of I, electrolysis was carried out at −0.66 V on a mercury pool electrode in the presence...
of a large excess of acetic acid ([H] = 8 µM, [HOAc] = 50 mM, pH 3.0). Formation of gas bubbles could be observed and evolution of H₂ was confirmed by gas chromatography. The charge accumulated over a period of one hour, after correction from the contribution of the blank solution, results in a turnover number (TON) of 52 moles of H₂ per mole of I (Fig. S5, ESI†). This TON value is a conservative underestimate that could be significantly increased by the utilisation of a larger separation frit and optimization of the cell surface area to volume ratio.

Since two protons are consumed for each H₂ molecule produced, measuring the increase in pH during electrolysis is an easy method to quantify the Faradaic efficiency of I. The rise of ca. 1.1 pH units observed after a 30 min electrolysis at −0.66 V of an acidified NaCl solution matches that calculated from the amount of charge consumed, establishing that I operates close to 100% Faradaic efficiency (Fig. S6, ESI†).

Polarogram and UV-visible spectrum recorded after electrolysis indicated no noticeable degradation of I. Control experiment showed a low catalytic activity when a fresh acidic electrolyte that does not contain I was added to a used mercury pool electrode rinsed once with water, indicating a slight adsorption of I during electrolysis (Fig. S5, ESI†). However no solid deposits were observed on the mercury surface, which remained shiny after extended experiments.

3.4. Mechanism of catalytic H₂ production mediated by I

Electrochemical measurements described above parallel those carried out in organic solvents. A practical advantage of working in an aqueous medium is that not only acid concentration but also pH can be easily altered. We evaluated the pH effect on the current–potential response of I by varying the relative proportion of H₃PO₄, H₂PO₄⁻ and HPO₄²⁻ while maintaining the total concentration of the electrolyte at 0.1 M (Fig. 5). Decreasing pH from 7.1 to 2.8 shifts positively the peak potential, consistent with an electrochemical reduction that involves protons. The slope \( \delta E/\delta \mathrm{pH} = 30 \text{ mV} (\sim 2.3 \text{ RT/2F}) \) suggests that the transfer of one proton is coupled to the transfer of two electrons. The peak current is not very responsive to pH over the range 7 to 6. The potential of the reduction peak shifts however positively, showing that the reduction of I is coupled with proton transfer even at neutral pH. The catalytic current increases by two orders of magnitude over the range 6 \( > \) pH \( > \) 3. This clearly indicates that the rate determining step of H₂ production is a protonation step. We also note that the catalytic current tends to level off at pH \( < \) 3, likely because of a change in the catalytic mechanism.

From these results and on the basis of literature precedent, we tentatively propose the catalytic cycle depicted in Scheme 2. Catalysis begins with the reduction of the binuclear FeᴵFeᴵᴵ compound I. Whether this reduction step involves two electrons as seen in organic solvents or only one electron is not established. In both situations, the electron transfer steps are coupled with a proton transfer step (oxidative addition of H⁺) leading to the putative hydride intermediate [Fe⁶⁻Fe⁷⁺(H)]⁺. In organic solvents, this Fe⁶⁻Fe⁷⁺-hydride intermediate is hardly protonated by strong acid, which explains the poor activity of I for H₂ production in acetonitrile for example. In contrast, in aqueous media, the Fe⁶⁻Fe⁷⁺-hydride intermediate is protonated at pH \( < \) 6 to release H₂ regenerating I and closing the catalytic cycle.

Fig. 5 Plots of the catalytic wave potential (top) and current enhancement (bottom) versus pH measured for 20 µM I in 0.1 M phosphate solution containing 10 mM SDS. pH was adjusted by varying the relative proportion of H₃PO₄, H₂PO₄⁻ and HPO₄²⁻. Peak potential and current were obtained by differential pulse polarography at a scan rate of 2.5 mV s⁻¹ and an amplitude of 50 mV.

Scheme 2 Proposed mechanism for the catalysis of electrochemical H₂ production mediated by I.

We postulate that the last protonation step is the rate determining step in agreement with the pH dependence of the catalytic current (Fig. 4).

4. Conclusions

In summary, we showed that the hydrophobic bdt-diiron derivative I can be easily dispersed in an aqueous SDS solution. Reproducible current–potential responses corresponding to the reduction of freely diffusing species were obtained over a large pH range at a dropping mercury electrode. The most striking result is the high catalytic activity of I for H₂ production in
water regarding its poor catalytic activity for the same reaction in organic solvent. Beyond the questions raised regarding the validity and relevance of the TOF value (2600 s⁻¹ at [acid] = 10 mM) obtained here by the Dubois’s treatment, the high activity of the bdt-diiron catalyst is clearly demonstrated by observation of current densities exceeding 0.5 mA cm⁻² at [I] = 60 µM and [acid]/[I] = 17. Another important result is that the bdt-diiron derivative I works at potentials positive to ~0.7 V at pH ≈ 3, corresponding to an overpotential |η| < 0.5 V that is competitive with those recently reported for the molecular cobalt pyridine catalysts producing H₂ at neutral pH.34,35

Furthermore, the electrochemical method described in this paper should permit extended investigation of diiron models in water without complications brought in by the synthesis of compounds holding hydrophilic ligands.

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Notes and references