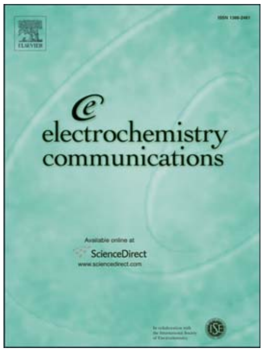

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Acridinium salts as metal-free electrocatalyst for hydrogen evolution reaction

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Abstract

Here we report the purely organic metal-free electrocatalyst − acridinium salt 9-phenyl-10-methylacridinium iodide for hydrogen evolution reaction. A controlled potential electrolysis experiment in present 9-phenyl-10-methylacridinium iodide with a simultaneous gas chromatographic analysis confirmed the catalytic production of molecular hydrogen. The behavior of the catalytic wave is typical for a "total catalysis". A mechanism involving initial reduction of $PhAcr^+/PhAcr^\bullet$ and subsequent protonation is proposed.

Keywords: Hydrogen evolution reaction, electrocatalytic reduction, metal-free electrocatalyst, total catalysis, acridinium salt

1. Introduction

Besides finding use in many industries such as petroleum refining, metal treatment and chemical production, molecular hydrogen has been declared a clean fuel of the future [1]. If produced by water electrolysis [2] powered from renewables, such as wind and solar [3], it might offer a solution to the increasing energy demands of an ever-growing human population and environmental sustainability.

One of the key obstacles towards making hydrogen production by water electrolysis economically feasible is the high cost associated with the catalysts used in industrial applications; these are often based on platinum, a precious metal of low abundance [4]. This triggered the search for new catalysts formed by earth-abundant elements [5], mostly by learning from natural enzymes, iron and/or nickel hydrogenases [6-7], that produce molecular hydrogen from water under ambient conditions with turnover frequencies reaching 9000 mole of H_2 per mole of catalyst per second [8]. Although hydrogenases themselves are so efficient in terms of high activity and low overpotentials, they are extremely sensitive to environmental conditions (temperature, pH, presence of oxygen) and are difficult to obtain in sufficient quantities for industrial purposes [9].

Most of these issues of high cost and low stability would be solved by designing a metal-free molecular catalyst ultimately made from earth-abundant elements (C, H, N, O). Note that hydrogenases were initially thought to be metal-free enzymes [10]; even though it turned out otherwise, this inspired further search for pure organic catalysts. Recently it has also been shown that some polysaccharides, such as chitosan, catalyze hydrogen evolution [11,12]. However, purely organic molecular compounds have never been viewed as electrocatalysts for hydrogen production.

Here we report metal-free electrocatalysts for generating hydrogen from acidic organic media. A controlled potential electrolysis experiment at −0.850 V versus Fc/Fc^+ confirms high reactivity and high fidelity in a 9-phenyl-10-

methylacridinium iodide in hydrogen evolution reaction from acidic organic media. The electrocatalyst is one of a family of acridinium compounds with a phenyl substituent at the 9 position (Scheme 1), which do not suffer from the radical dimerization common for the unsubstituted acridinium [13]. The findings provide clear evidence that, like precious metals, well-designed metal-free counterparts have great potential for highly efficient electrocatalytic HER, thus opening a new avenue towards replacing noble metals by alternatives in a wide variety of applications.

2. Material and methods

2.1. Synthesis

9-phenyl-10-methylacridinium iodide (PhAcrI) was obtained as described previously [13] by quaternization of 9-phenylacridine with methyl iodide in a sealed tube for 10 hours. The purity of the compound, assessed by NMR and elemental analysis, was estimated as more than 99.6%.

2.2. Cyclic voltammetry

Cyclic voltammetry experiments were carried out in acetonitrile solutions (with 0.1 M [n-Bu_4N][BF_4] as a supporting electrolyte) using a model Parstat 2273 potentiostat with a conventional one-compartment three-electrode cell (10 ml of solution). A glassy carbon electrode (GCE) with an active surface area of 0.125 cm^2 was used as a working electrode. The electrode was thoroughly polished and rinsed before and between the measurements. A platinum counter electrode and a standard Ag/AgCl reference electrode were used. Conversion to other reference electrodes is as follows: the ferrocene Fc^+/Fc couple lies at 0.41 V versus Ag/AgCl in acetonitrile. All the solutions were thoroughly deaerated by passing argon through them before the cyclic voltammetry experiments and above them during the measurements.

2.3. Controlled potential electrolysis in acetonitrile.

10 ml of acetonitrile solution of $HClO_4$ (150 mM), PhAcrI (1 mM) and [n-Bu_4N][BF_4] (0.1 M) was electrolyzed for 60 min at –850 mV (related to Fc^+/Fc). A glassy carbon electrode (GCE) with an active surface area S= 0.125 cm^2 was used as a working electrode. The production of molecular hydrogen was confirmed by gas chromatography.

2.4. Gas chromatography

Gas chromatography analysis of the gases evolved during the electrolysis was performed with a Varian 450 gas chromatograph equipped with a pulsed discharge helium ionization detector D-4-I-VA38-R. Hydrogen production was quantitatively detected using a stainless steel column 30 m in length with inside diameter 250 µm at 120°C for the detector and at 80°C for the oven. The carrier gas was helium flowing at a rate of 40 ml min^{-1}. The injections (250 µL) were performed *via* a sampling loop. The retention time of gaseous H_2 was 2.48 min.

3. Results and discussion

Cyclic voltammograms for PhAcrI in acetonitrile (Figure 1) at a glassy carbon electrode (GCE) show a reversible one-electron reduction wave at –0.86 V versus Fc/Fc^+, and this is assigned to a redox couple $PhAcr^+$/$PhAcr^•$ [13]. Note that the values reported for cyclic voltammograms are the experimental peak potentials; the potentials at half of the catalytic current are used below to calculate overpotentials [14] and to perform electrolysis experiments.

Addition of perchloric acid to this solution results in an increase in the reduction current and in the disappearance of a reverse wave $PhAcr^•$/$PhAcr^+$ (Figure 1), suggesting catalytic reduction of protons to molecular hydrogen. The behavior of the catalytic wave at different acid-to-catalyst concentration ratios is typical for a “total catalysis” [15]: at a lower ratio, it occurs at potentials more positive than that of the couple $PhAcr^+/PhAcr^\bullet$ and shifts to more negative potentials as this ratio becomes higher. Cyclic voltammetry experiments performed in the absence of PhAcrI show no signs of electrocatalysis; introducing a “used” GCE into a fresh electrolyte without PhAcrI also does not result in any electrocatalytic activity. This implies a truly homogeneous catalysis with no significant adsorption or decomposition of the catalyst on the surface of an electrode. Note that the shape of all the cyclic voltammograms does not reach a plateau even at scan rates up to 10 V s^{-1} or at high concentrations of both perchloric acid (up to 0.1 M) and PhAcrI (up to 12.5 mM), which is a sign of a fast catalytic process limited by the diffusion of the substrate to the electrode surface.

A controlled potential electrolysis experiment at −0.850 V versus Fc/Fc^+ for one hour with a simultaneous gas chromatographic analysis confirmed the catalytic production of molecular hydrogen at an overpotential of 0.82 V. The latter value is calculated as a difference between the thermodynamic potential for proton reduction in an acetonitrile solution of perchloric acid and the observed potential at half of the catalytic current [16, 17]. A one-hour electrolysis of 10^{-6} mol PhAcrI in acetonitrile led to the evolution of 7.6×10^{-7} mol of molecular hydrogen (electric charge 0.14 C, Faradaic yield 35±5). The low Faradaic yield is probably due to side electrochemical or chemical reactions. Indeed, according to the 1H and 13C{1H} NMR spectra obtained after one-hour electrolysis is observed the signals starting 9-phenyl-10-methylacridinium iodide and additionally 9-phenyl-10-methyl-9,10-dihydroacridine. The proposed catalytic cycle for the generation of H_2 mediated by 9-phenyl-10-methyl-9,10-dihydroacridine is shown in Figure 2. The first step in this mechanism includes the reduction of the cations $PhAcr^+$ to the radical species $PhAcr^\cdot$, which was unambiguously identified using the potential of the one-electron reduction wave (–0.86 V versus Fc/Fc^+) in the cyclic voltammograms of PhAcrI [13]. At −0.850 V (the potential used for electrocatalytic hydrogen production), no further reduction of the resulting radicals $PhAcr^\cdot$ to the anions PhAcr- by the EEC pathway can take place, as it occurs at a significantly more negative potential (−1.73 V versus Fc/Fc^+). So the second step is the protonation of the radicals $\mathrm{PhAcr}^{\cdot}$, which we propose to involve the nitrogen atom as the most Lewis basic site in $\mathrm{PhAcr}^{\cdot}$. The initial cations PhAcr^{+} are quantitatively regenerated during the process so there is no need for the second electrochemical reduction to produce molecular hydrogen. This is similar to a classic hemolytic pathway for proton reduction catalyzed by a transition metal-based electrocatalyst. At present, more detail is studied electrocatalytic mechanism.

Figure 1 (inset) shows the ratio of catalytic current in the presence of perchloric acid ($i_{\mathbf{cat}}$) to the peak current for the reduction of PhAcrI in the absence of acid ($i_{\mathbf{p}}$) as a function of the acid concentration in the experiment. At concentrations of less than 60 equiv of perchloric acid to (relative to catalyst), the observed catalytic current increased with acid concentration. Beyond this acid concentration, no significant increase in catalytic current was observed (Figure 1). This type of behavior is expected when substrate (H^{+}) concentration is sufficiently high that it is not depleted by the catalytic process during the course of the experiment and some other elementary step becomes rate limiting in the catalytic cycle. Using data in this acid independent regime, the rate constant for hydrogen evolution (k_{obs}) can be calculated from the expression:

$$\frac{i_{cat}}{i_p} = \frac{2}{0.4463}\sqrt{\frac{RTk_{obs}}{F\upsilon}}, \qquad (1)$$

in which ν is the potential scan rate, n is the number of electrons transferred (two for hydrogen evolution), R is the universal gas constant, T is the temperature, and F is Faraday’s constant. The $i_{\mathbf{cat}}/i_{\mathbf{p}}$ values of ≈3 in the acid independent region (for a scan rate of 100 mV s^{-1}) indicate an acid independent rate constant of 1.12 s^{-1}. Repeating this analysis using independent data sets generated using different electrochemical potential scan rates indicates that the TOF is a robust parameter in the range 1.12 − 1.13 s^{-1}. Note that in the absence of an extended plateau region for j_{max}, eq 1 provides only an approximation of k_{obs} in the present system [17]. Alternatively, the catalytic current-enhancement parameter, reflecting the efficiency of the electrocatalytic process, expressed as the i_{cat}/i_p ratio with i_{cat} being the catalytic current and i_p the peak current associated with a monoelectronic wave of the catalyst, is used as a proxy for the turnover frequency [18]. The resulting i_{cat}/i_p for PhAcrI value of ≈3 (Fig. 1 inset) is higher than that for any reported complex, such as $[Fe_2(S_2C_3H_6)\text{-}(CO)_3(dppv)(NO)]^+$ [dppv = cis-1,2-bis(diphenylphosphinoethylene)], $(\mu\text{-}SC_6H_4\text{-}2\text{-}(CO)S\text{-}\mu)[Fe_2(CO)_6]$ and $(\mu\text{-}pdt)[Fe_2(CO_5)PPyr_3]$ [pdt = propanedithiolate; PPyr = tripyrrolylphosphine)]

(in all case $i_{cat}/i_p < 2$), for complex $\mu\text{-}pdt[Fe(CO)_3][Fe(CO)_2IMes]$ [IMes =1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene] the i_{cat}/i_p ratio ≈3 [18] . The i_{cat}/i_p value exhibited by PhAcrI is, however, lower than those of some molecular Ni/Co systems in organic solvents: $[(dmgBF_2)_2Co(MeCN)_2]$ [dmg = dimethylglyoxime]

(i_{cat}/i_p≈30); $[(PPh_2NPh)_2Ni]^{2+}$ (≈38); $[(P^{tBu}{}_2NPh_2)Co(MeCN)_3]^{2+}$ (≈40) [18]. It should be noted that the potentials of the electrocatalytic processes in the presence of such complexes are significantly shifted in the cathodic region compared to PhAcrI. So for $(\mu\text{-}SC_6H_4\text{-}2\text{-}(CO)S\text{-}\mu)[Fe_2(CO)_6]$ E = –1.3 V (vs Fc/Fc^+) and for $(\mu\text{-}pdt)[Fe_2(CO_5)PPyr_3]$, and $\mu\text{-}pdt[Fe(CO)_3][Fe(CO)_2IMes]$ E = –1.3 V and –1.9 V(vs Fc/Fc^+), respectively.

4. Conclusions

In summary, we have shown that a metal-free electrocatalyst, a simple acridinium salt, demonstrates promising catalytic activity in electrochemical hydrogen evolution from acidic organic media. The electrocatalytic activity of 9-phenyl-10-methylacridinium iodide was studied in acetonitrile solutions: addition of $HClO_4$ to these solutions produced a catalytic wave at the reduction potential that is characteristic of the electrocatalytic process of the hydrogen evolution reaction. Further studies are in progress to optimize the reaction conditions for efficient hydrogen production by varying the electronic properties of the 9-phenyl-10-methylacridinium iodide catalyst.

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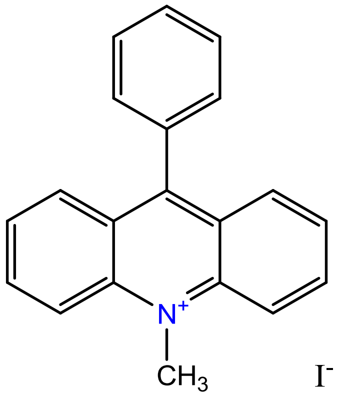
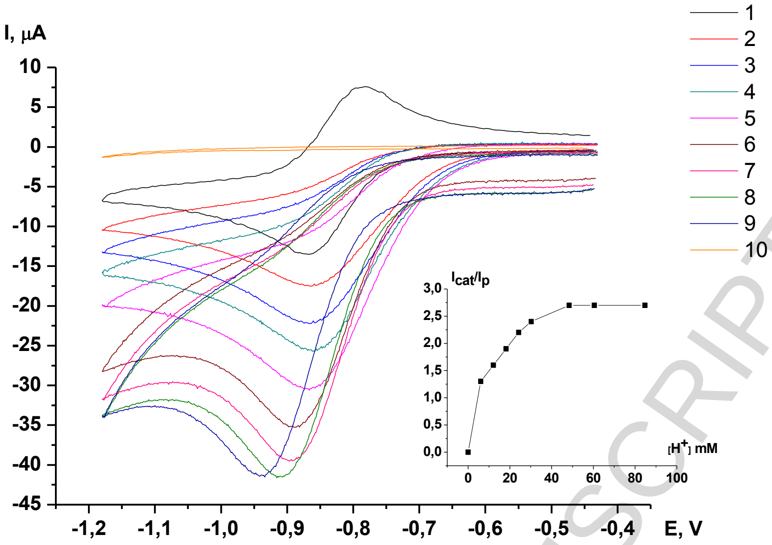


Scheme 1.

Figure 1. Cyclic voltammogramsfor 1.0 mM solutions of PhAcrI in acetonitrile at a concentration of perchloric acid (in mM) increasing from top to bottom: 0 (**1**), 6.05 (**2**), 12.1 (**3**), 18.15 (**4**), 24.2 (**5**), 30.25 (**6**), 48.4 (**7**), 60.5 (**8**), 84.7 (**9**), and perchloric acid (concentration of 84.7 mM) in the absence of PhAcrI (**10**). Conditions: scan rate 200 mV s^{-1}, 25°C, 0.1 M [*n*-Bu_4N][BF_4] in acetonitrile, glassy carbon working electrode. Potentials are referenced to Fc/Fc^+. **Inset:** Dependence of the i_{cat}/i_p on the concentration of $HClO_4$ mM at a scan rate 200 mV s^{-1} in 1.0 mM solutions of PhAcrI in acetonitrile.

Figure 2. Tentative catalytic mechanism for proton reduction by PhAcrI with alternative EEC and ECEC pathways; counter-ions are omitted for clarity. The potentials are given for acetonitrile solution and are referenced to Fc/Fc^+.



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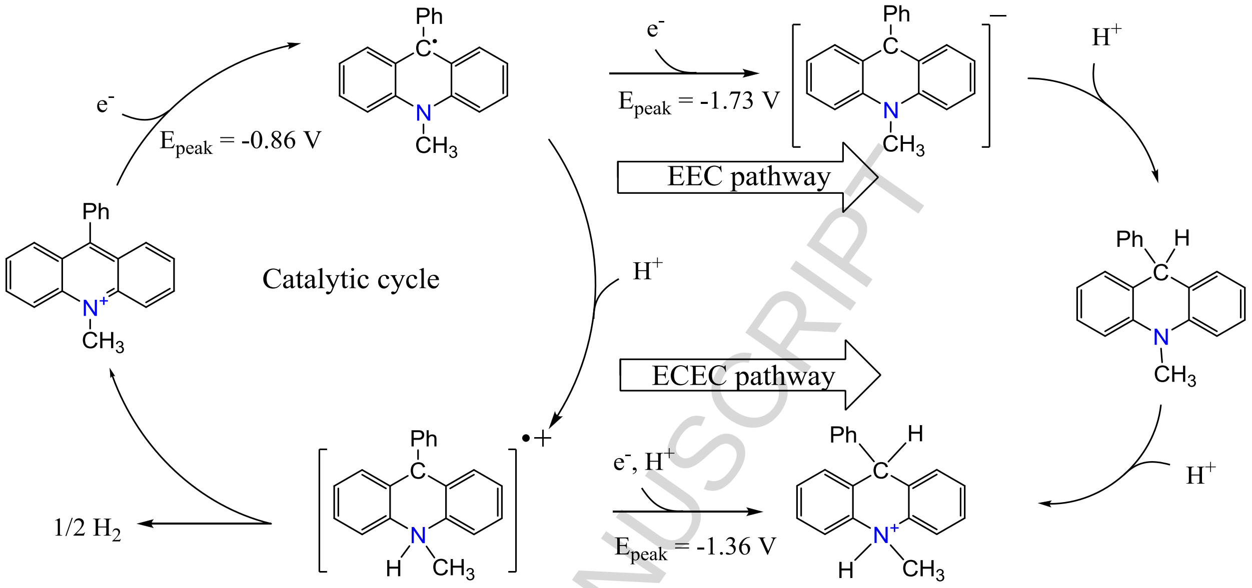

Figure 2. Tentative catalytic mechanism for proton reduction by PhAcrI with alternative EEC and ECEC pathways; counter-ions are omitted for clarity. The potentials are given for acetonitrile solution and are referenced to Fc/Fc$^+$.

Highlights

- Acridinium salts are electrocatalysts for H_2 production.

- Tentative catalytic mechanism of proton reduction by PhAcrI is discussed.

- A mechanism involving initial reduction of $PhAcr^+/PhAcr^{\bullet}$ and subsequent protonation is proposed.