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H_2 Evolution and Molecular Electrocatalysts: Determination of Overpotentials and Effect of Homoconjugation

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In an effort to standardize the determination of overpotential values for H_2-evolving catalysts in non-aqueous solvents and allow a reliable comparison of catalysts prepared and assayed by different groups, we propose to adopt the half-wave potential as reference potential. We provide a simple method for measuring it from usual stationary cyclic voltammograms, and we derive the formulas to which the measured potential should be compared, taking into account the effect of homoconjugation. We also revisit tabulated values of the standard reduction potential of protons in non-aqueous solvents, $E^\circ_{H^+/H_2}$.

Introduction

Hydrogen production, through the reduction of water (eq 1), appears as the most convenient way to allow for a durable storage of renewable energies. In that context, electrocatalysis is the enabling technology and the development of original electrocatalysts as alternatives to the use of platinum the requisite for this approach to become economically viable.[1]

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad (1)$$

Until recently, hydrogenases[2] have been the unique example of catalysts exclusively based on earth-abundant metals rivaling platinum when adsorbed onto carbon-based electrodes.[3] Their direct utilization as electrode material for practical applications is however hindered by their sensitivity to O_2[4] and the difficulty to scale up their production. Our approach, and that of many other groups, is not to directly incorporate hydrogenases into biotechnological devices but rather to use them as an inspiration for designing efficient noble metal-free inorganic complexes with catalytic activities for proton reduction and/or hydrogen oxidation.[5−7] Many such bioinspired complexes have been synthesized, mostly over the past decade, and have been assayed for their catalytic activity (or lack thereof) under various experimental conditions.

The goal of this approach is to graft these molecular catalysts onto electrode materials, a strategy that has recently proved successful for producing catalytic materials with potential for use in technological devices.[8,9] However, considering the huge amount of work necessary for grafting, in terms of chemical derivatization and characterization of the electrode material, there is a strong requirement for a first screening of the catalysts based on solution studies. Turnover frequencies, turnover number, and electrocatalytic potential are the most commonly used parameters to evaluate the performances of molecular catalysts. However, because catalysts are generally assayed in different conditions, another key phenomenological parameter to evaluate molecular catalysts and compare their energetic efficiencies is their overpotential for H_2-evolution; this parameter is a measure of the energy lost in driving reaction 1 at a significant rate as compared to the thermodynamic limit[10] and is thus directly related to the efficiency of the energetic transduction process. It is important to state here that the term "overpotential" has two common accepted

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uses that are conceptually very different.[11,12] For surface electrochemists studying electrode materials or surfaces modified with nanodeposits or enzymatic electrocatalysts, the overpotential ($\eta = E - E_{eq}$) is just a convenient measure of the extent of the polarization. In that context, the overpotential quantifies the driving force of the electrochemical reaction and is the relevant parameter to be used on the abscissa in a free energy correlation diagram, as formalized by Tafel.[12] However, when the electrochemical reaction is kinetically limited, as is the case for eq 1 on most common electrode materials but Pt,[13] it does not occur at potential values one would predict from thermodynamics and instead, considerably higher electron energies (more negative potentials) must be applied to make the reaction occur at a measurable rate.[11] The additional potential (beyond the thermodynamic requirement) needed is also called the overpotential and relates here to an activation energy.[14] This second definition is the relevant one for characterizing molecular electrocatalysts as a measure of the activation barrier for the reaction and thus a threshold for the appearance of catalysis. In that case, the overpotential is thus a kinetic parameter essential for the evaluation of a given catalyst. So far however, no well-defined methodology has been established for the case of a catalyst in solution, which leads to difficulties in comparing the properties of different catalytic compounds synthesized by different groups.[15]

Assaying the activity of a H_2-evolving catalyst always involves a classic voltammetric technique, most of the time cyclic voltammetry at a stationary electrode, performed with increasing quantities of a weak acid used as a proton source. The electrochemical response changes upon the addition, with the appearance of an irreversible catalytic wave that corresponds to proton reduction. There is no standard method for experimentally determining a “reduction potential” for this irreversible wave: depending on the authors, it is defined either as the position of the “onset” (the earliest observable event of catalysis), of the peak (where the fastest rate of catalysis is observed) or that for which half of the maximum current is obtained; it can be seen in Figure 1 (top panel) that on a practical example the variability in the determination method can lead to differences of up to 200 mV in the measured value for a given voltammogram. To determine the overpotential, one must compare this measured potential value to the theoretical one computed in the case of an electrochemically reversible process. In general, this value is simply assimilated to the standard potential of reduction of the acid that can be computed from tabulated data.[10] Unfortunately, the exact value of $E^\circ_{H^+/H_2}$ in solvents is debated, with discrepancies of up to 100 mV between electrochemical[10] and thermochemical[16,17] approaches. While that was acceptable earlier, greater adherence to well-defined and accurate methods and standards is becoming necessary now that more and more catalysts are announced with small overpotentials.[8,17–24] In particular, care should be taken when using acids displaying homoconjugation, a phenomenon in which the conjugate base is stabilized by hydrogen bond to the acid, as it increases their acidity at high concentrations and leads to significant overestimation of the performances of the catalysts in terms of overpotential. While this phenomenon has been known for more than half a century,[25] it has never been taken into account in the context of catalytic H_2-evolution, even though it affects

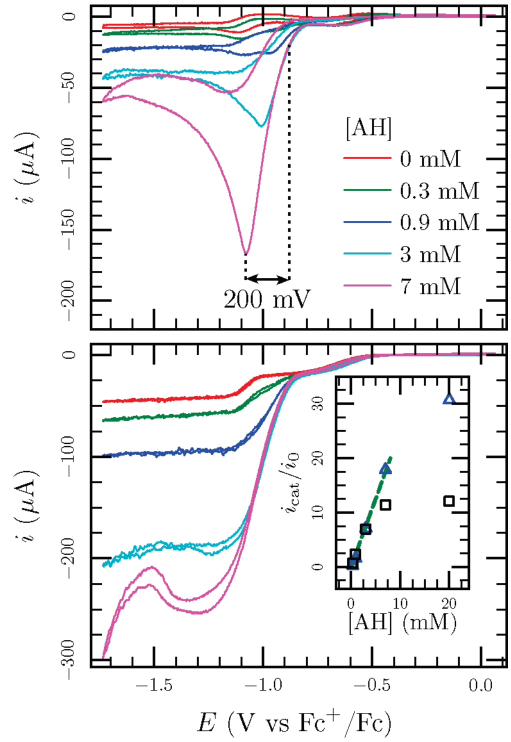

Figure 1. Cyclic voltamograms of 0.3 mM of [Co(DO)(DOH)pnBr_2] at a glassy carbon electrode in acetonitrile in the presence of increasing quantities of anilinium. Voltammograms show that the addition of acid leads to the appearance of an irreversible wave of increasing amplitude corresponding to the reduction of anilinium catalyzed by the complex. Conditions: $T = 298$ K, scan rate 100 mV/s. Supporting electrolyte: acetonitrile with 0.1 M Bu_4NPF_6. Top: stationary electrode; bottom: RDE, rotation rate 1 krpm. That the forward and backward scans superimpose for RDE experiments shows that the system is permanently at steady-state. Anilinium concentrations as indicated (same for both graphs). Inset: catalytic enhancement i_{cat}/i_0 for stationary (blue triangles) and rotating (black squares) electrodes, as a function of anilinium concentration. The dashed green line materializes the linearity range at low concentrations. In the upper panel, the horizontal arrow shows the difference between catalytic potential values measured at the “peak” or the “onset” of the catalytic wave (about 200 mV).

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most of the acids used in acetonitrile, which itself is the most commonly used solvent for studying H_2-evolution catalysts.

In this paper, we have chosen to standardize on the half-wave potential. We show that, even though it has no particular physical significance, it is a reliable point to define the electrochemical potential related to hydrogen evolution catalyzed by molecular complexes; we derive the formulas that allow for the determination of the overpotential and reconcile the tabulated data regarding the standard potential of the H^+/H_2 couple in non-aqueous solvents.

Materials and Methods

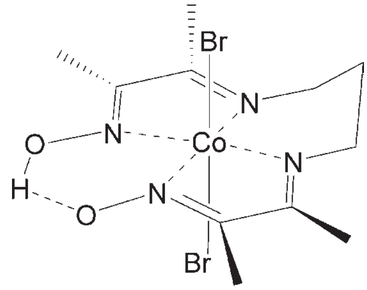
Electrochemical analysis was performed using an EG&G potentiostat, model 273A. Both stationary and rotating disk electrode (RDE) voltammetric experiments were carried out in a three-electrode electrochemical cell under nitrogen atmosphere, using glassy carbon RDE as working electrode (surface 7 mm^2). The auxiliary electrode was a platinum grid. The reference electrode was based on the Ag/AgCl/KCl 3 M couple. All potentials given in this work are quoted relative to the ferricinium/ferrocene (Fc^+/Fc) couple, whose potential was measured in the cell at the end of each experiment. The experiments were conducted in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. Additions of acid were done by syringe from solutions of the acid in the same electrolyte. Trifluoroacetic acid was obtained from Sigma (purity ≥98%) and used without further purification. Anilinium tetrafluoroborate was obtained by the reaction of HBF_4 with aniline in ether. [Co(DO)(DOH)pnBr_2], where {(DO)(DOH)pn} is the deprotonated form of N^2,$N^{2\prime}$-propanediylbis(2,3-butanedione 2-imine 3-oxime), was synthesized as described previously.[18] Electrochemical simulations (described in the Supporting Information) were done using the DigiElch software.[26] Analysis of the voltammetric traces (sigmoidal fit, derivation, and peak finding) was performed using the program SOAS.[27]

Results

Determination of Overpotentials for Homoconjugation-Free Acids. For the sake of simplicity, we will restrict the scope of this paper to acids that do not protonate the solvent to a significant extent at concentrations commonly used in H_2-evolution assays, that is, with $pK_a \geq 6$.[28] This is the case for the vast majority of acids used to characterize H_2-evolving catalysts.

First, we will demonstrate how it is possible to extract relevant potentials from the voltammetric curves, using the cobalt diimine dioxime complex [Co(DO)(DOH)pnBr_2] (Scheme 1) as an example. We have recently shown that this catalyst displays excellent activity with relatively small overpotentials.[18] We have proposed that catalysis proceeds as follows: electrogenerated Co(I) binds a proton to form Co(III)-H and the latter likely reacts with another Co(III)-H to form H_2 and Co(II). Figure 1 shows voltammograms of the reduction of the acid anilinum tetrafluoroborate catalyzed by [Co(DO)(DOH)pnBr_2]. We can see that, as the acid concentration increases, an irreversible reduction wave that corresponds to the catalytic reduction of the acid appears at potentials more positive than the Co(II)/Co(I) reversible wave.

Scheme 1. Structure of the Diimine-Dioxime Cobalt Complex [Co(DO)-(DOH)pnBr_2]



A parameter commonly used to quantify catalytic activity is the ratio of the current in the catalytic wave over that of the Co(II)/Co(I) monoelectronic wave observed in the absence of acid, i_{cat}/i_0; this parameter is sometimes referred to as "catalytic enhancement" and is used as a proxy for the turnover frequency that can be determined analytically only in very specific cases.[29] It is shown in the inset in the bottom panel of Figure 1. Here, we do not seek to analyze quantitatively this parameter, but rather to approximately define two catalytic regimes: in the low acid concentration range, the catalytic enhancement depends linearly on the acid concentration, which means that the catalytic rate is limited by mass transport, while at higher concentration the catalytic enhancement saturates as catalysis is no longer rate-limited by the mass transport of acid but rather by the instrinsic turnover frequency of the catalyst itself.[30] This first linear region is important since it defines the conditions for a reliable determination of the overpotential (see below).

The determination of the overpotential from catalytic voltammograms such as those shown in Figure 1 consists in taking the potential value at a well-defined point on these voltammograms and comparing it to the corresponding theoretical values for an electrochemically reversible process. The most easily identifiable point on RDE voltammograms is that for which the catalytic current is half the maximum current; we will name the corresponding potential $E^E_{1/2}$. This parameter can be read directly on experimental RDE voltammograms. For greater precision, it can be obtained by fitting the catalytic wave to a sigmoid:

$$i = i_1 + \frac{i_2}{1 + \exp\left[\frac{\alpha F}{RT}(E - E^E_{1/2})\right]} \qquad (2)$$

where i_1, i_2, α, and $E^E_{1/2}$ are the parameters of the fit.[31]

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[28] We have, however, derived the expression for acids that do not undergo homoconjugation without restriction on pK_a in the Supporting Information; we do not discuss the results here to avoid confusing the reader.

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[30] The original paper by Nicholson and Shain on catalytic voltammograms[45] also refers to a linearity range of i_{cat}/i_0 in which certain equations are valid; both ranges are completely unrelated, as here we plot the catalytic enhancement as a function of the acid concentration, while Nicholson and Shain plotted it as a function of $(k/v)^{1/2}$, k being the first-order catalytic rate constant and v the scan rate.

[31] α doest not need to be an integer. For the reversible reduction of an acid at an electrode, the difference in molecularity between reactants and products results in a very complex shape (see equations in the Supporting Information); fitting this dependence by a sigmoid gives a reasonable fit for a value of α around 0.8.

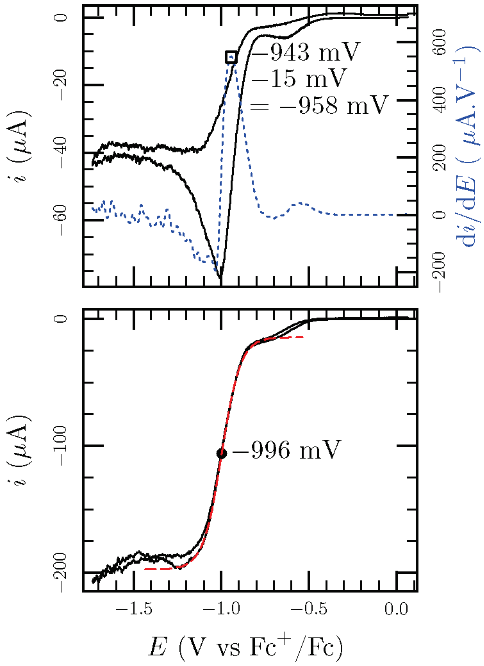

Figure 2. Demonstration of the methods available for the determination of $E^E_{1/2}$ from experimental curves. In both panels, the black line is the recorded voltammogram. The dotted blue line is the first derivative of the forward scan (its values read against the right-hand-side axis). In the bottom panel, the red dashed line is a fit to eq 2. The position of the maxima of the derivative is indicated by an open square; that of the inflection point of the sigmoid by a circle. These symbol's meanings match those of Figure 3. To obtain $E^E_{1/2}$ from the stationary cyclic voltammogram (top panel), 15 mV should be subtracted from the potential of the maximum of the derivative. Conditions: 3 mM anilinium tetrafluoroborate, 0.3 mM [Co(DO)(DOH)pnBr$_2$], T = 298 K, scan rate 100 mV/s. Top panel: stationary electrode. Bottom panel: RDE, rotation frequency 1 krpm.

This parameter can also be obtained from usual stationary cyclic voltammograms: simulations of ideal cyclic voltammograms similar to those conducted by Treimer and Evans[32] (in the Supporting Information) showed that the maximum of the first derivative of the forward scan, that is, the inflection point, in stationary voltammograms is systematically 15 mV higher than the value predicted for the half-wave potential in RDE experiments under the same conditions (see Supporting Information, Figure S2); it is therefore possible to obtain $E^E_{1/2}$ from stationary cyclic voltammograms by subtracting 15 mV from the potential of the maximum of the first derivative of the forward scan. These two methods for measuring $E^E_{1/2}$ are exemplified in Figure 2; they give the following values: −958 mV (stationary electrode) and −996 mV (RDE).

This measured potential should be compared to the value for a reversible process; ideally, a reference potential should be measured under the same conditions with a reversible electrode. Unfortunately, there is no such electrode, as even platinum fails to give reversible waves with most acids in acetonitrile (data not shown), excepted in very specific conditions (using HClO$_4$ and Pt microelectrodes for instance). These conditions were exploited by Daniele and co-workers[33] to tabulate values of $E^\circ_{H^+/H_2}$ in various solvents. In this context, the method used by all the groups that have reported overpotentials for H$_2$-evolving catalysts is to estimate a theoretical value for a reversible process based on tabulated data. Here, we derive an equation to rigorously compute the theoretical half-wave potential, to which $E^E_{1/2}$ should be compared: the potential for which half the maximum acid reduction current is obtained for an ideal electrode, at which reaction 3 is electrochemically reversible:

Table 1. Values of the Physico-Chemical Constants Necessary to Compute Potentials Using Formula 8

solvent	$E^\circ_{H^+/H_2}$	$C^\circ_{H_2}$	ε_D
acetonitrile	−0.07 V	3.3 mM[36]	40 ± 5 mV
DMF	−0.62 V	1.9 mM[36]	40 ± 5 mV
dimethylsulfoxide	−0.67 V	1.1 mM[37]	40 ± 5 mV

The hydrogen solubility is often given in the literature as a mole fraction χ_{H_2} for 1 bar. To obtain $C^\circ_{H_2}$, we used the following formula: $C^\circ_{H_2} = \chi_{H_2} \times \rho/M$, where ρ is the density of the solvent and M its molar mass. (ρ should be expressed in g m^{-3} and M in g mol^{-1} to obtain $C^\circ_{H_2}$ in mM.) The values of $E^\circ_{H^+/H_2}$ were computed from ref 33 using the method described in Supporting Information and outlined in the section "Standard Potential of Proton Reduction in Solvents".

$$\mathrm{AH} + \mathrm{e}^- \rightleftharpoons \mathrm{A}^- + \frac{1}{2}\,\mathrm{H}_2 \qquad (3)$$

This electrode in thermodynamic equilibrium with reaction 3 has a potential given by the Nernst equation (eq 4).

$$E = E^\circ_{\mathrm{AH/H_2,A^-}} + \frac{RT}{F}\ln\left[\frac{[\mathrm{AH}]}{[\mathrm{A}^-]}\left(\frac{p_0}{p_{\mathrm{H_2}}}\right)^{1/2}\right] \qquad (4)$$

where [AH] and [A$^-$] are respectively the concentration of the acid and its conjugate base, p_{H_2} is the partial pressure of hydrogen (all three values taken in the immediate vicinity of the electrode), $p_0 = 10^5$ Pa. $E^\circ_{AH/H_2,A^-}$ is the standard potential of the AH/A$^-$,H$_2$ couple and is related to the dissociation constant of AH through eq 6.[10]

$$\mathrm{AH} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+_{(\mathrm{solvated})} \qquad 10^{-pK_a} \qquad (5)$$

$$E^\circ_{\mathrm{AH/H_2,A^-}} = E^\circ_{\mathrm{H^+/H_2}} - \frac{2.303 \times RT}{F}\,\mathrm{p}K_\mathrm{a} \qquad (6)$$

where $E^\circ_{H^+/H_2}$ is the standard potential for the reduction of protons in the solvent considered (see discussion in the next section; tabulated values are summarized in Table 1) and 10^{-pK_a} is the dissociation constant of the acid.

In the scope of this paper, it is more interesting to rewrite eq 4 in terms of the concentration of dissolved hydrogen, [H$_2$], rather than its partial pressure:

$$E = E^\circ_{\mathrm{AH/H_2,A^-}} + \frac{RT}{2F}\ln\left(\frac{[\mathrm{AH}]^2 C^\circ_{\mathrm{H_2}}}{[\mathrm{A}^-]^2[\mathrm{H_2}]}\right) \qquad (7)$$

where $C^\circ_{H_2}$ is the concentration of dissolved hydrogen corresponding to a partial pressure of 10^5 Pa.

Obtaining the theoretical half-wave potential, $E^T_{1/2}$, is only a matter of computing the concentrations of AH, A$^-$, and H$_2$ that give rise to half the maximum current in RDE voltammograms and injecting them into eq 7. We present in the Supporting Information a rigorous analytical treatment for the case when no A$^-$ nor H$_2$ is initially present in the electrolyte. It shows that in that case

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Table 2. Commonly Used Acids and the Relevant Constants Used for Computing the Half-Wave Potentials, Taking into Account Homoconjugation When Applicable[a]

acid	solvent	pK_a	$\log_{10}K_C$	E_{ref} (V vs Fc+/Fc)		
				1 mM	10 mM	100 mM
perchloric acid	CH_3CN	2.1	$-\infty$[b]		pK_a too low[c]	
DMFH$^+$	CH_3CN	6.1	$-\infty$[b]	−0.38 V	−0.41 V	−0.44 V
p-cyanoanilinium	CH_3CN	7.0	≤0.6[d]	−0.43 V	−0.46 V	−0.49 V
sulfuric acid	CH_3CN	7.5	3.3	−0.44 V	−0.41 V	−0.38 V
tosic acid	CH_3CN	8.3	2.9	−0.51 V	−0.48 V	−0.45 V
hydrochloric acid	CH_3CN	8.9	2.2	−0.54 V	−0.56 V	−0.53 V
methanesulfonic acid	CH_3CN	10.0	3.8	−0.56 V	−0.53 V	−0.50 V
trichloroacetic acid	CH_3CN	10.6	2.5	−0.64 V	−0.64 V	−0.61 V
anilinium	CH_3CN	10.7	0.6	−0.65 V	−0.68 V	−0.71 V
trifluoroacetic acid	CH_3CN	12.7	3.9	−0.71 V	−0.68 V	−0.65 V
triethylammonium	CH_3CN	18.6	0	−1.11 V	−1.14 V	−1.17 V
benzoic acid	CH_3CN	20.7	3.6	−1.20 V	−1.17 V	−1.14 V
acetic acid	CH_3CN	22.3	3.7	−1.29 V	−1.26 V	−1.23 V
perchloric acid	DMF				complete dissociation	
hydrochloric acid	DMF	3.2	2.2		pK_a too low[c]	
HBF_4	DMF	3.4	$-\infty$[b]		pK_a too low[c]	
phosphonic acid	DMF	9.0	3.6	−1.07 V	−1.04 V	−1.01 V
triethylammonium	DMF	9.2	$-\infty$[b]	−1.12 V	−1.15 V	−1.18 V
p-nitrobenzoic acid	DMF	10.6	2	−1.20 V	−1.23 V	−1.20 V
benzoic acid	DMF	12.2	2	−1.29 V	−1.32 V	−1.29 V
acetic acid	DMF	13.5	2	−1.37 V	−1.40 V	−1.37 V

[a] E_{ref} is the half-wave potential of the most acidic couple in solution (see text). Values for other concentrations can be obtained using eqs 8 and 14. Most of the constants come from the comprehensive compilation by Izutsu,[39] except for *p*-cyanoanilinium.[42] A constant ratio of $D_{H_2}/D_{AH} = 10$ was assumed for the computations, based on typical values of diffusion coefficients (see Supporting Information). [b] This acid is not known to undergo homoconjugation in this solvent. [c] The pK_a of this acid is below the 6, which is out of the scope of this paper; in particular, eqs 8 and 14 do not apply. The reader can refer to Supporting Information where the complete derivation is available for homoconjugation-free acids without restriction on pK_a. [d] The homoconjugation constant was not determined for *p*-cyanoanilinium. However, since it is less basic than anilinium, it is expected that the K_C constant will be lower than that of anilinium.

$E^T_{1/2}$ is given by

$$E^T_{1/2} = E^\circ_{H^+/H_2} = -\frac{2.303 \times RT}{F}pK_a + \varepsilon_D - \frac{RT}{2F}\ln\frac{C_0}{C^\circ_{H_2}} \qquad (8)$$

where C_0 is the total concentration of acid (i.e., the one injected by the experimenter into the electrolyte) and ε_D is a measure of how fast is the diffusion of the products with respect to that of the reactant:

$$\varepsilon_D = \frac{RT}{3F}\ln\frac{8{D_{A^-}}^2 D_{H_2}}{{D_{AH}}^3} \qquad (9)$$

D_i being the diffusion coefficient of species *i*. In general, the acid and its conjugated base will have very similar diffusion coefficients, so ε_D essentially reflects the difference in diffusion coefficients of the acid and H_2. Values of the physicochemical constants used in eq 8 for various solvents are given in Table 1. Exact determination of the ε_D parameter is difficult, as it depends on both the solvent and the acid considered. However, diffusion coefficients of H_2 in solvents[34] are typically of the order of 10^{-4} cm^2 s^{-1} while that of acids are expected to be in the 10^{-6} cm^2 s^{-1} to 10^{-5} cm^2 s^{-1} range.[35] Considering that ε_D depends only weakly on the diffusion coefficients, this allows for an estimation of ε_D of 40 ± 5 mV. Values of the pK_a are given in Table 2.

We show in the Supporting Information that it is also possible to compute the theoretical value of $E^T_{1/2}$ when A^- and/or H_2 are initially present in the electrolyte, but it leads to a significantly more complex formula. We therefore recommend against performing the voltammetric experiments under an atmosphere of H_2, and, similarly, in the presence of A^-.

Determining the overpotential is only a matter of comparing $E^E_{1/2}$ to $E^T_{1/2}$. This has been done in Figure 3. From the comparison of the experimental points (symbols) to the theoretical values (thick black line), one can determine the overpotential for the reduction of anilinium using [Co(DO)(DOH)pnBr_2] as the catalyst. One can see that in the concentration range where the catalytic enhancement i_{cat}/i_0 depends linearly on the concentration (materialized as a horizontal black line), the overpotential is essentially constant around 290 ± 20 mV. Outside of the linear range, the overpotential is greater; this suggests that for acids that do not display homoconjugation, overpotentials should better be measured with acid concentrations within the linearity range of the catalytic enhancement.

Standard Potential of Proton Reduction in Solvents. The standard potential of proton reduction in acetonitrile is subject to controversy: DuBois and co-workers, using a thermochemical approach based on the work of Wayner and Parker[38] propose values of $E^\circ_{H^+/H_2}$ versus Fc$^+$/Fc in the range −80 mV to −50 mV.[16,17] Daniele and co-workers, using a direct electrochemical approach, proposed a value of −260 mV,[33] that was later corrected for the incomplete dissociation of $HClO_4$ in acetonitrile to −140 mV by Evans and co-workers.[10] In a theoretical work presented in the Supporting Information, we have found that this discrepancy between "electrochemical" and "thermochemical" values is

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(34) Ross, M.; Hildebrand, J. H. *J. Chem. Phys.* **1964**, *40*, 2397–2399.
(35) Longsworth, L. G. *J. Colloid Interface Sci.* **1966**, *22*, 3–11.
(36) Brunner, E. *J. Chem. Eng. Data* **1985**, *30*, 269–273.
(37) Dymond, J. H. *J. Phys. Chem.* **1967**, *71*, 1829–1831.
(38) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287–294.

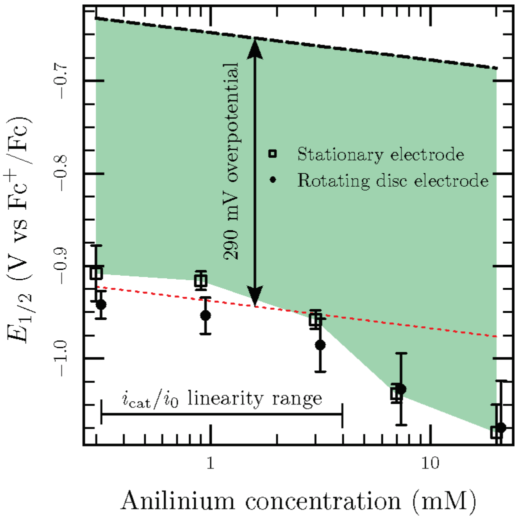

Figure 3. Values of $E^E_{1/2}$ for the catalytic reduction of anilinium by [Co(DO)(DOH)pnBr$_2$] measured using two different methods (sigmoidal fit for the RDE experiments and first derivative for stationary voltammograms) as a function of anilinium concentration. The thick dashed black line represents the theoretical value of $E^T_{1/2}$; the red dotted line represents a constant overpotential of 290 mV. The light green region represents the overpotential; for the sake of comparison with Figure 6, only data obtained using the stationary electrode are considered for this region. The horizontal black line represents the linearity range of the i_{cat}/i_0 parameter, as shown on the inset of Figure 1. Note the logarithmic scale for concentrations.

not due to the difference in experimental setups, but rather to flaws in the interpretation of electrochemical data.

Daniele and co-workers have assumed that the half-sum of the potentials of the forward and reverse peaks of the reduction of HClO$_4$ is the standard potential of the couple H$^+$/H$_2$; this is the case for most of the usual redox couples used at an electrode, but not for the H$^+$/H$_2$ couple as the change in molecularity between the reactants and the products for the electrode reaction induces a dependency of the potentials on the acid concentration. Partial dissociation of HClO$_4$ in acetonitrile adds yet another source of error, as noticed by Evans and co-workers.[10] Using the rigorous analytical treatment provided in the Supporting Information for the reduction of acids without restriction on their pK_a, we found that the correction to apply to Daniele's data to obtain $E^\circ_{H^+/H_2}$ is about +190 mV; this gives a corrected value of −70 mV, in perfect agreement with thermochemical values proposed by DuBois and co-workers. A correction of about the same magnitude was also computed for the values values for dimethylformamide (DMF) and dimethylsulfoxide (DMSO) given in Table 1.

Influence of Homoconjugation. Often, an acid (AH) and its conjugated base (A$^-$) form stable adducts (AHA$^-$) through hydrogen bonding[25] (reaction 10); this phenomenon is very frequent in acetonitrile, and present to a lesser extent in DMF.[39] It is called homoconjugation[40] and is quantified by the association constant K_C:

$$AH + A^- \rightleftharpoons AHA^- \qquad K_C \qquad (10)$$

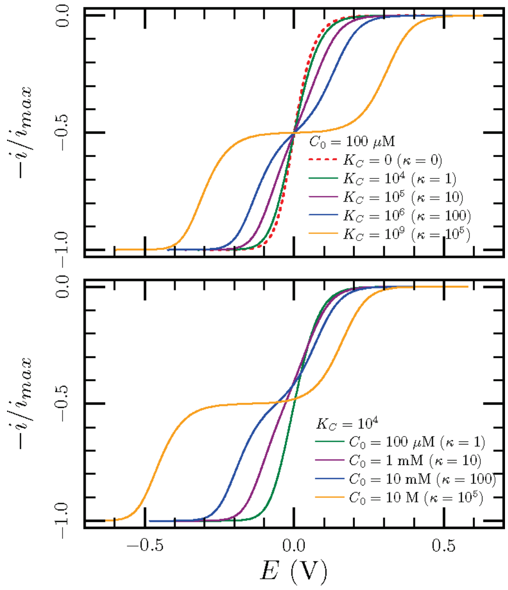

Figure 4. Theoretical profiles of current against potential for different values of the κ parameter. The upper panel shows the influence of K_C alone with a constant total concentration of acid; this shows how acids with different values of K_C would compare at the same concentration. The lower panel shows the influence of C_0 alone with a constant K_C; that is what happens in a typical experimental setup where acid concentration is increased over time by successive additions. The other parameters were chosen to have $E^T_{1/2}$ = 0 V for 100 μM.

This reaction displaces the acid base equilibrium (eq 5) in favor of the release of protons and therefore tends to increase the acidity of AH for concentrations well above $1/K_C$, where a significant portion of the homoconjugate AHA$^-$ is formed. Homoconjugation commonly occurs for most of the (weak) acids used in H$_2$-evolving assays in acetonitrile, and with some acids in other solvents, such as phosphonic acids in DMF and phenols in DMSO.[41]

For a total acid concentration of C_0, the extent of homoconjugation can be quantified using the simple nondimensional parameter

$$\kappa = K_C C_0 \qquad (11)$$

When κ is significantly lower than 1, C_0 is well below the $1/K_C$ threshold mentioned above and homoconjugation does not occur to a significant extent. Conversely, when κ is much greater than 1, reaction 10 is quantitative in the direction of the formation of the homoconjugate adduct.

Reaction 10 strongly affects the concentrations of the species involved in determining the electrode potential in eq 4. Just as for the case of simple acids, we have derived the relation between current and electrode potential for the case of an ideal RDE (Supporting Information). Figure 4 shows theoretical curves for different conditions. These theoretical curves show that in the low κ range ($\kappa < 1$), the wave corresponding to the reduction of the acid resembles that without homoconjugation ($\kappa = 0$, drawn as a dotted red line in Figure 4, upper panel); however, as κ increases, this single wave progressively splits into two reduction subwaves. First derivatives of the current−potential

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(39) Izutsu, K. *Acid-Base Dissociation Constants in dipolar aprotic solvents*; Chemical Data Series 35; Blackwell Scientific Publications: Cambridge, MA, 1990.

(40) Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005–5010.

(41) See Table 2 for the most commonly used acids; the reader is encouraged to refer to ref 39 for a more comprehensive list.

(42) Appel, A. M.; Lee, S.-J.; Franz, J. A.; DuBois, D. L.; Rakowski DuBois, M.; Twamley, B. *Organometallics* **2009**, *28*, 749–754.

curves display two clearly defined maxima for values of κ above 10. Further analysis presented in Supporting Information, Figure S1 shows that the first, high-potential, wave corresponds to the reduction of the acid to the homoconjugate adduct:

$$2\mathrm{AH} + \mathrm{e}^- \rightleftharpoons \mathrm{AHA}^- + \frac{1}{2}\,\mathrm{H}_2 \qquad (12)$$

and the second, low-potential, wave to the reduction of the homoconjugate adduct:

$$\mathrm{AHA}^- + \mathrm{e}^- \rightleftharpoons 2\mathrm{A}^- + \frac{1}{2}\,\mathrm{H}_2 \qquad (13)$$

For $\kappa > 10$, the half-wave potential (for which current is respectively 1/4 and 3/4 of its maximum value) of each of these subwaves is given by the approximative expressions:

$$\begin{aligned} E^{\mathrm{T}}_{1/2(\mathrm{AH/AHA^-})} &= E^{\circ}_{\mathrm{H^+/H_2}} - \frac{2.303 \times RT}{F}\,\mathrm{p}K_{\mathrm{a}} + \varepsilon_{\mathrm{D}} \\ &\quad + \frac{RT}{2F}\ln(2K_C{}^2 C_0 C^{\circ}_{\mathrm{H_2}}) \qquad (14) \end{aligned}$$

for the first wave and

$$\begin{aligned} E^{T}_{1/2(\mathrm{AHA^-/A^-})} &= E^{\circ}_{\mathrm{H^+/H_2}} - \frac{2.303 \times RT}{F}\,\mathrm{p}K_{\mathrm{a}} + \varepsilon_{D} \\ &\quad + \frac{RT}{2F}\ln\frac{2C^{\circ}_{\mathrm{H_2}}}{3K_C{}^2 C_0{}^3} \qquad (15) \end{aligned}$$

for the second one. The potential of the first wave shifts *up* by about 30 mV by decade of concentration, while that of the second shifts *down* by about 90 mV by decade (Figure 4, lower panel). Suprisingly, the potential for which the current is half of its maximal value is still given by formula 8, even when homoconjugation has notable effects; this is materialized in Figure 4, upper panel, by the fact that all curves intersect at $E^T_{1/2}$ (0 V on the figure). However, as κ increases, it becomes more and more ill-defined, since it corresponds to a point between two reduction waves, and not to the well-defined middle of a unique wave: it is therefore irrelevant for the determination of the overpotential of a catalyst. Table 2 gives the constants necessary to compute $E^T_{1/2\ (\mathrm{AH/AHA^-})}$, $E^T_{1/2}$, and $E^T_{1/2\ (\mathrm{AHA^-/A^-})}$ for acid/solvent couples commonly used to evaluate $\mathrm{H_2}$-evolving catalysts.

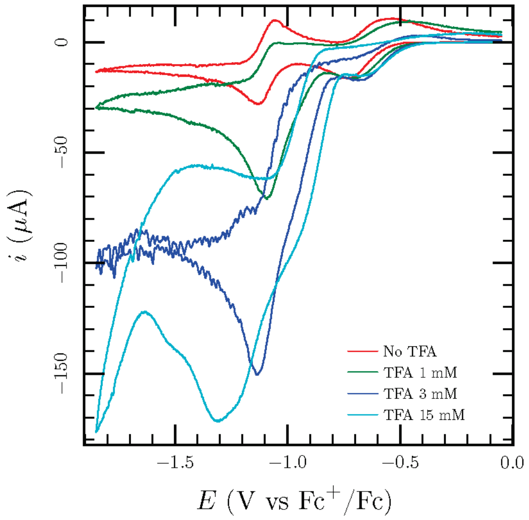

Figure 5. Cyclic voltammograms of [Co(DO)(DOH)pnBr$_2$] (0.4 mM) at a stationary glassy carbon electrode in acetonitrile in the presence of increasing quantities of trifluoroacetic acid (TFA). Conditions: T = 298 K, electrolyte: acetonitrile with 0.1 M of hexafluorophosphate tetrabutylammonium salt, scan rate 100 mV/s, TFA concentrations as indicated.

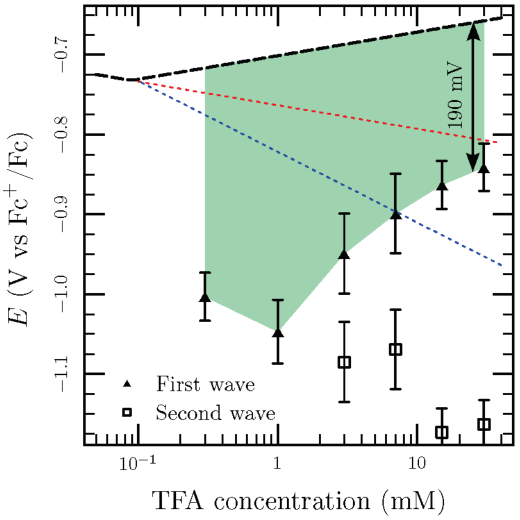

Figure 6. Half-wave potentials of the waves observed on the voltammograms at a stationary electrode shown in Figure 5, measured using the “first derivative” technique highlighted above (the 15 mV offset was taken into account). The half-wave potential of the first or only wave is shown as black triangles, while that of the second is shown as open squares when present. The black dashed line corresponds to E_{ref}, to which the potential of the first wave should be compared to determine the overpotential (see text). The red dotted line is the theoretical prediction of eq 8, while the dotted blue line is that of eq 15. The light green region represents the overpotential for the reduction of TFA. Note the logarithmic scale for concentrations.

We have recorded cyclic voltammograms using stationary electrodes and RDEs with trifluoroacetic acid as proton donor, and [Co(DO)(DOH)pnBr$_2$] as catalyst. Trifluoroacetic acid (TFA) displays a high value of $K_c = 10^{3.9}$ (see Table 2), and is therefore expected to undergo homoconjugation to a significant extent even at low concentrations: the κ parameter is about 10 for 1 mM of acid. Results are shown in Figure 5. Just as for anilinium, the addition of acid leads to the appearance of an irreversible reduction wave at potentials slightly more positive than that of the Co(II)/Co(I) wave. However, unlike anilinium, this wave splits when the acid concentration increases (i.e., when κ becomes greater than 10). The second wave is only visible on voltammograms using stationary electrodes and is obscured in RDE experiments by the direct reduction of TFA at the electrode (data not shown). The half-wave reduction potential was measured for both waves using the derivative of the cyclic voltammograms recorded using a stationary electrode; the results are shown in Figure 6, along with the values predicted by eqs 8, 14, and 15. They show that the measured half-wave potentials qualitatively follow the trends predicted by the theoretical analysis: the potential of the first wave first decreases when only one wave is visible and then increases when both waves become visible. That of the second wave always decreases. This confirms that the first wave corresponds to the reduction of the acid to $\mathrm{H_2}$ and the homoconjugate adduct (eq 12), and the second to the reduction of the homoconjugate adduct (eq 13). To obtain the overpotential, one need to compare the half-wave potential of the first wave (highest potential) to E_{ref}, the half-wave potential of the most acidic couple in solution, which is given by the *maximum* of $E^{T}_{1/2}$ and $E^{T}_{1/2\ (\mathrm{AH/AHA^-})}$ (E_{ref} is represented by a thick dashed black line in Figure 6). The overpotential is materialized in Figure 6 by a colored region. One can see that in the case where homoconjugation dominates, it is not possible to determine unambiguously a value of overpotential that would characterize the catalyst in the presence of the acid and the solvent considered, as the values strongly depend on the concentration of the acid. In the high concentration range, the overpotential for the reduction of TFA is about 190 mV, which means that [Co(DO)(DOH)pnBr_2] is a better catalyst for the reduction of TFA than it is for anilinium.

It would be tempting to compare the potential of the second measured wave to $E^{T}_{1/2\ (\mathrm{AHA^-/A^-})}$ to have another determination of the overpotential. This would not be correct, however, as the concentration of the species in the potential range where the second wave is observed is strongly affected by the occurrence of the first one; as a consequence, the potential of the second wave is unlikely to report on reaction 13 alone.

Discussion

The overpotential for proton reduction is a phenomenological parameter widely used since the 2006 tutorial article by Felton and co-workers,[10] to evaluate the efficiency of H_2-evolution catalysts. While it does not provide any insights about mechanistic aspects, which require much deeper studies,[43] it is commonly thought that for a given catalyst, assayed with a given acid in a given solvent, there is a unique value of overpotential that allows comparison between distinct catalysts and/or assay conditions. Our results support this notion for certain conditions. However, its precise and reliable determination suffers from two problems: first, the method used to obtain the catalytic potential from electrochemical experiments varies according to the authors; often the exact method is not even disclosed. Our group used to take the peak potential of the catalytic reduction wave in well-defined conditions (1 mM catalyst, 3 mM acid);[18,23] some groups use the "onset" of the catalytic wave,[44] or the potential of the redox system involved in the catalysis, measured in the absence of acid, however, arguing that catalysis occurs at the same potential;[19,20] others take the potential where the current is half its maximum value.[21]

As was noticed by Nicholson and Shain,[45] the peak potential is ill-defined in catalytic systems because peaks are broad or sometimes even completely absent.[22] The "onset" of the catalytic wave, defined as the point where the catalytic current deviates from the background current, cannot be used as it is an empirical point whose potential cannot be computed for theoretical curves.[46] Just like Nicholson and Shain[45] we therefore have chosen as a reference the "half-wave" potential, the one for which the current is half of the maximum catalytic current at a RDE, as it is well-defined and easy to identify using voltammetry at a RDE. More practically, it can also be obtained using stationary electrode cyclic voltammetry by taking the potential of the maximum of the first derivative of the forward scan and *subtracting* 15 mV.[47] We have shown that both methods give comparable results within about 30 to 40 mV.

The second problem that hinders the determination of the overpotential regards the computation of the theoretical value to which measured potentials should be compared. Evans and co-workers have proposed that measured potentials should be compared to the standard potential of the AH/H_2,A^- couple ($E^{\circ}_{\mathrm{AH/H_2,A^-}}$, given by eq 6), arguing that this is the potential corresponding to half of the maximum current. While this is true as a first approximation, our results show that, even for an acid concentration comparable to the solubility of H_2 in the solvent, this leads to underestimating the overpotential (i.e., overestimating the performance of the catalyst) by $\varepsilon_{\mathrm{D}} \approx 40$ mV, *for homoconjugation-free acids*. Moreover, eq 8 shows that the theoretical value for the half-wave potential decreases as concentration increases of about 30 mV by decade. This had not been noticed before, but it is not surprising since reaction 3 gives 3 moles of products for 2 moles of reactant; its thermodynamics are therefore expected to depend on the total concentration of the species, contrary to usual reduction processes, which only involve eletron-transfer steps.

In reference 18 we announced an overpotential for the reduction of anilinium catalyzed by [Co(DO)(DOH)pnBr_2] of 200 mV at 3 mM acid concentration. Data points in Figure 3 yield an overpotential of 290 ± 20 mV. This discrepancy comes from two partly counterbalancing errors in our earlier work: (i) the potential measured was that of the peak, which is lower than that of the inflection point (we announced -0.97 V in ref 18, while we read -0.95 V in Figure 1 for voltammograms at a stationary electrode); (ii) the theoretical value used was wrong, first because we used the value of $E^{\circ}_{\mathrm{H^+/H_2}}$ proposed in ref 10, which we now know wrong, and second both because ε_{D} and the concentration dependence was not taken into account: we used the $E^{\circ}_{\mathrm{AH/H_2,A^-}} = -0.77$ V in ref 18, while we now compute $E^{T}_{1/2} = -0.66$ V for 3 mM anilinium).

Our results show that the overpotential is somewhat ill-defined (Figure 3) and depends on the catalytic regime. This is not surprising since it is a kinetic parameter, which means that it is sensitive to changes in the kinetic conditions (such as changes in concentrations). In particular, for large concentrations of acid, the catalytic rate saturates; our results show that in these conditions, the gain in catalytic rate is obtained at the expense of energetic efficiency. This is, however, an important result of the present study that comes in contradiction with the common notion that overpotential is a unique parameter that characterizes a catalyst. Nevertheless, we show that a unique value of overpotential can be measured reliably for homoconjugation-free acids in the concentration range where catalysis is rate-limited by mass-transport of acid to the electrode.While theoretical foundations of such an assessment are still to be established, this sets a new empirical standard for the experimental determination of overpotential.

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[43] Savéant, J.-M. *Chem. Rev.* **2008**, *108*, 2348–2378.

[44] Berben, L. A.; Peters, J. C. *Chem. Commun.* **2010**, *46*, 398–400.

[45] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

[46] Equation 14 from the Supporting Information can be simplified at low x values (high potentials) to give the following expression for the current: $i = 2^{-1/3} i_{\mathrm{max}} \exp[(3/2RT)(E^{T}_{1/2} - E)] > 0$.

[47] Though this correction may seem small with respect to the indetermination of the overpotential, it is a systematic error easy to correct, and therefore should be taken into account.

A quick glance at eq 7 might induce one to believe that introducing H_2 or A^- into the electrolyte leads to terms canceling out in the fraction and therefore of a half-wave potential of $E^\circ_{AH/H_2,A^-}$; theoretical computations presented in Supporting Information show otherwise: far from simplifying the equation giving the half-wave potential, it makes it significantly more complex, except when the acid concentration is much lower than the solubility of H_2 in the solvent, that is, for acid concentrations not greater than 300 μM in acetonitrile. We therefore discourage the use of an H_2 atmosphere for overpotential determination or the introduction of the acid under the form of a AH/A^- "buffer". It is important to note, however, that performing experiments in the presence of H_2 and/or A^- can provide useful mechanistic insights.

Homoconjugation greatly complicates the thermodynamics of H_2 evolution. As there are two proton sources, AH and AHA^-, present in the electrolyte, two consecutive waves of equal amplitudes are observed on the voltammograms (Figure 4). They correspond respectively to the reduction of AH to AHA^- (eq 12 for the first wave) and of AHA^- to A^- (eq 13 for the second), both concomitant to a production of molecular hydrogen; potentials measured between these waves have no physicochemical meaning. Whether the two waves are observed experimentally or not depends on the catalyst used and the conditions; for instance, $[Co(DO)(DOH)pnBr_2]$ displays both reduction waves (Figure 5) while only the first one is visible on a platinum RDE (data not shown). The observability of the second wave is a matter of kinetics: it is possible that within the homoconjugate adduct, the labile proton is much less accessible to the catalyst than it is in the free acid. In any case, when using an acid in conditions where homoconjugation plays an important role (for $\kappa \geq 1$), one must compare the highest potential measured on experimental waves to the half-wave potential of the most acidic couple, E_{ref}, the maximum of $E^T_{1/2}$ and $E^T_{1/2\ (AH/AHA^-)}$; this thermodynamic reference is plotted as a thick dashed black line on both Figure 3 and Figure 6, and its value has been calculated in Table 2 for different concentrations for acids commonly used as proton source for H_2-evolving assays.

For acids that undergo homoconjugation to a significant extent, using the standard potential of the $AH/A^-,H_2$ couple as the reference potential thus leads to large underestimations of the overpotential for the reduction of acids (i.e., overestimations of the catalyst's capacities). One example of such an underestimation comes from our group: in ref 18, Table 2, we compared the values of the position of the catalytic wave for the reduction of TFA to the standard reduction potential of TFA (given by eq 6, −0.89 V vs Fc^+/Fc, using the value of $E^\circ_{H^+/H_2}$ from ref 10), which lead to the puzzling observation that $[Co(DO)_2BF_2pnBr_2]$ is operating at the thermodynamic limit. In the present work, we show that the experimental potential[48] should have been compared to the value given by eq 14, that is, −0.70 V. Surely this catalyst has low overpotentials for the reduction of TFA (about 190 mV), but not to the point of being thermodynamically reversible. The same applies for $[Co(dmgBF_2)_2(H_2O)_2]$[23] or $[Co(dmgBF_2)_2(CH_3CN)_2]$[20] ($dmgH_2$ is dimethylglyoxime) assayed under similar conditions. Similarly, it is likely that quite a few overpotentials of complexes for the reduction of acids displaying homoconjugation announced in the literature are affected by this problem and need to be revised upward. On the other hand, homoconjugation resulted in a large underestimation of the measured potential for the reduction of TFA by $[Co(DO)(DOH)pnBr_2]$, determined as −1.10 V in ref 18: as the two reduction waves widely overlap for 3 mM acid (see the dark blue trace in Figure 6), the potential of the peak we measured in ref 18 was in fact that of the second reduction wave. Using the derivative of the voltammogram, both waves are visible (Figure 6), which in turn gives higher measured half-wave potential (−0.95 V in Figure 5). The overpotential hardly changed, however, with respect to what we published earlier as the theoretical reference potential did shift up by about the same amount, because of the new value of $E^\circ_{H^+/H_2}$ and the recognition of the effects of homoconjugation. On a practical point of view, the derivative of the voltammograms offer a very effective diagnostic of the presence of two waves. One should keep in mind, when using homoconjugation-prone acids, that the overpotential strongly depends on the concentration of acid used.

Summary and Outlook

Studying H_2 evolution in non-aqueous solvents is flawed by two common misconceptions. First, acids in solvents behave very differently than acids in water; one example of such a difference is the homoconjugation phenomenon. The second problem is the molecularity change in eq 3, as it induces a dependence of measured potentials on substrate concentration, unlike most couples studied by electrochemists. This second problem appears to have been ignored so far for H_2-evolution, and in particular led to incorrect tabulated values of $E^\circ_{H^+/H_2}$.

We have investigated the determination of overpotentials of catalysts for the reduction of protons, and we propose a simple method to obtain overpotentials from experimental data. We have chosen the half-wave potential as a reference as it is both easy to obtain from experimental curves and easy to compute theoretically. The half-wave potential for the catalytic reduction of an acid in the absence of H_2 and of its conjugated base can either be directly measured using a RDE, or, more practically, obtained from the potential of the maximum of the first derivative of the forward scan of stationary cyclic voltammograms and subtracting 15 mV. This value should then be compared to the theoretical value for the most acidic couple present in solution: either $E^T_{1/2}$ (eq 8) for homoconjugation-free acids, or the maximum of $E^T_{1/2\ (AH/AHA^-)}$ (eq 14) and $E^T_{1/2}$ for acids displaying homoconjugation. This value is based on the standard potential of proton reduction in the solvent, $E^\circ_{H^+/H_2}$: we have shown that some of the reported values are incorrect; corrected values are presented in Table 1. For convenience, values of the reference potential for various acids can be directly read in Table 2 for concentrations of 1, 10, and 100 mM. Overpotential should be measured in the acid concentration range where the catalytic enhancement depends linearly on the acid concentration. We found that the overall uncertainty in determining the overpotential is of the order of 40 mV.

Homoconjugation significantly complicates the determination of overpotentials; homoconjugation-prone acids should be avoided if possible for assaying H_2-evolution catalysts, though this may prove difficult when using acetonitrile as solvent. We suggest the use of DMF where this problem is much less frequent.

It is our hope that this paper will pave the way for a standardization of the measurement and computation of overpotentials

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(48) Or, more exactly, the potential obtained using the experimental data through the method of the derivative outlined above for stationary electrodes.

in non-aqueous solvents; this would avoid biases introduced by the variability in their determination and make it possible to reliably compare catalysts synthesized and assayed by different groups.

Acknowledgment. The authors acknowledge the Technological Research Division of CEA (p**H$_2$**oton project), the French National Research Agency (ANR, Grant 07-BLAN0298-01) and Carnot funding for financial support.

Supporting Information Available: The derivation of eqs 8, 14, and 15, the equation for the theoretical curves of Figure 4, the demonstration of the attribution of the two reduction waves for high values of κ, the equation for the half-wave potential in the presence of H_2 and/or A^-, the equation for the half-wave potential without restriction on acid pK_a, the detailed discussion of the literature values of $E^{\circ}_{H^+/H_2}$, the description of the simulations of cyclic voltammograms, and supplementary Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.