

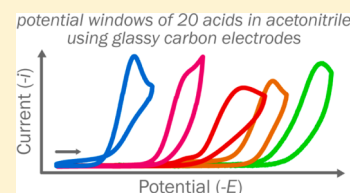
Electrochemical Reduction of Brønsted Acids by Glassy Carbon in Acetonitrile—Implications for Electrocatalytic Hydrogen Evolution

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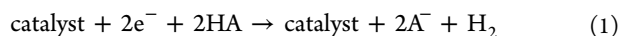
Supporting Information

ABSTRACT: Molecular catalysts for electrochemically driven hydrogen evolution are often studied in acetonitrile with glassy carbon working electrodes and Brønsted acids. Surprisingly, little information is available regarding the potentials at which acids are directly reduced on glassy carbon. This work examines acid electroreduction in acetonitrile on glassy carbon electrodes by cyclic voltammetry. Reduction potentials, spanning a range exceeding 2 V, were found for 20 acids. The addition of 100 mM water was not found to shift the reduction potential of any acid studied, although current enhancement was observed for some acids. The data reported provides a guide for selecting acids to use in electrocatalysis experiments such that direct electrode reduction is avoided.



INTRODUCTION

Homogeneous hydrogen evolution catalysts are often evaluated electrochemically in acetonitrile, where an electrode supplies electrons and a Brønsted acid (HA) provides protons.



A possibly serious complication in these studies is direct acid reduction by the electrode at potentials that overlap with molecular catalysis (Figure 1).



It has been noted that the catalytic currents observed for some catalysts may have contributions arising from direct substrate reduction.¹ As accurate extraction of kinetic data from catalytic cyclic voltammograms relies on the observed current,² competing direct reduction complicates kinetic analysis. Direct reduction of substrate can also yield cyclic voltammograms (CVs) that mimic prototypical catalytic responses,³ especially those of catalysis exhibiting substrate depletion,⁴ making it unclear whether the catalyst is responsible for the current enhancement. As many hydrogen-evolution catalysts operate at fairly cathodic potentials, the possibility of direct acid reduction by both relatively strong and relatively weak acids becomes an even greater concern.

These issues are minimized when acid-only controls are run. Unfortunately, acid-only cyclic voltammograms are not always reported with catalytic data. The widespread use of glassy carbon working electrodes for nonaqueous hydrogen-evolving catalysts may provide one reason. Glassy carbon is often cited as noncatalytic,^{5–7} incorrectly implying that the direct reduction of protons to form hydrogen occurs at such negative potentials as to be inconsequential. While glassy carbon indeed reduces acids at more negative potentials than platinum,⁸ reduction processes can still occur. Moreover, when stronger acids are employed, reduction is expected to occur at relatively positive potentials.¹ While aqueous proton reduction has been

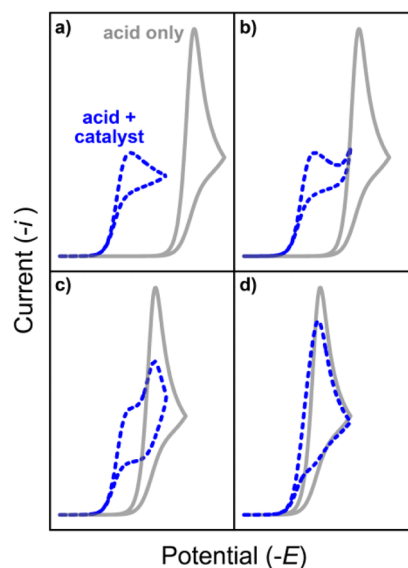


Figure 1. Simulated cyclic voltammograms of an EC' catalytic process in which direct substrate reduction (acid reduction) occurs at potentials (a) far from catalysis, (b) slightly overlapping with catalysis, (c) strongly overlapping with catalysis, and (d) nearly completely overlapping with catalysis. Solid gray line indicates that only acid is present, while the dotted blue line indicates that catalyst and acid are present. Simulated using DigiElch electrochemical simulation software (Gamry Instruments); $\alpha = 0.5$, $k_s = 10\,000\text{ cm}^2/\text{s}$, $k_{\text{catalysis}} = 10\,000\text{ M}^{-1}\text{ s}^{-1}$, $[\text{catalyst}] = 0.01\text{ M}$, $[\text{substrate}]_0 = 5\text{ M}$.

extensively studied on many electrode materials, especially platinum,^{9,10} and remains the subject of active research,¹⁰ little data is available on the reduction of acids in acetonitrile by glassy carbon. One report described the use of different

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electrodes to achieve wider potential windows for acids in acetonitrile, but only data for acetic acid was shown.⁸

Water, whether intentionally added or present as contamination, is a further complication. Dramatic increases in catalytic current have been reported for some catalysts in acetonitrile with added water.^{11,12} For some of these cases, water has been suggested to act as a proton relay capable of more easily reaching the metal centers of sterically crowded molecular catalysts. Water has been noted to shift the reduction potential of perchloric acid on mercury cathodically by hundreds of millivolts, having stabilized the acidic species against reduction.¹³ It is unclear whether the reduction potentials of weaker acids could be affected as well, potentially resulting in overlapping direct reduction in the potential regime of a catalyst.

Motivated by our interest in molecular electrocatalysts for hydrogen evolution, we were interested in better understanding the potential window limits of glassy carbon (GC). Accordingly, the goal of this work is to establish useful approximate working ranges for common acids in acetonitrile for the specific purpose of catalytic hydrogen evolution. Reduction potentials of 20 acids in acetonitrile on GC are reported along with details on the influence of water.

EXPERIMENTAL SECTION

General Considerations. Acetonitrile (Fisher Scientific, HPLC grade, >99.9%) and diethyl ether (Fisher Scientific, >99%) were degassed with argon and dried using a Pure Process Technology solvent system. Aniline (Sigma-Aldrich), 4-chloroaniline (Aldrich, 98%), 4-*tert*-butylaniline (Sigma-Aldrich, 99%), 4-nitroaniline (Sigma-Aldrich, 99%), 4-methoxyaniline (Alfa-Aesar, 99%), 4-bromoaniline (Acros Organics, 96%), *N,N*-dimethylaniline (Sigma-Aldrich, 99%), tetrafluoroboric acid diethyl ether complex (Aldrich), benzoic acid (Aldrich, 99%), silver nitrate (Aldrich, 99+%), phenol (Sigma-Aldrich, >99%), pyridinium chloride (Alfa Aesar, 98%), *p*-toluenesulfonic acid (Sigma-Aldrich, >98.5%), trichloroacetic acid (TCI America, >99%), triethylammonium chloride (Aldrich, 98%), trifluoromethanesulfonic acid (Acros Organics, 99%), 2-nitrophenol (Alfa Aesar, 98%), 3-nitroaniline (TCI, >98%), methyl orange (Aldrich), water for polishing (Fisher Scientific, HPLC grade), and 200 proof ethanol (Decon Laboratories, Inc.) were used as received. Salicylic acid (Aldrich) was recrystallized from boiling distilled tap water, filtered, washed with cold water, and dried under vacuum at 85–90 °C for 14 h. Tetrabutylammonium hexafluorophosphate (TCI, >98%) was recrystallized from hot ethanol, filtered, washed with cold ethanol, and dried at room temperature under vacuum for 19 h. Dimethylformamide triflate was prepared as reported.¹⁴ Acetic acid (Fisher Scientific, 99.9%) and triethylamine (Acros, 99%) were dried over activated 3 Å molecular sieves and degassed with three freeze–pump–thaw cycles. The triethylamine was further dried by passage through activated alumina and by storage over activated 3 Å molecular sieves. Trifluoroacetic acid (Sigma-Aldrich, 99%) and water (from a Milli-Q system) were degassed with three freeze–pump–thaw cycles. CD₃CN (Cambridge Isotopes Laboratories, Inc., 99.8%) was degassed with three freeze–pump–thaw cycles, passed through activated alumina to remove water, and stored over activated 3 Å molecular sieves. Elemental analysis was performed by Atlantic Microlabs, Inc. NMR spectra were recorded on a Bruker 400 MHz spectrometer and referenced to proteo solvent impurities.¹⁵ UV–vis spectra were recorded in a nitrogen-filled glovebox using fiber optic cables connected to an Agilent Cary 60 UV–vis spectrophotometer.

Syntheses. Syntheses were performed in a nitrogen-filled glovebox. While syntheses of some of the aniliniums reported here have been reported previously,^{16,17} these reports lacked some details as well as NMR and elemental analyses to confirm purity. The general procedure was as follows: To a rapidly stirring 5 mL solution of diethyl ether containing 1.0 g of the respective substituted aniline (3 g in the case of aniline itself) was added 0.95 mol equiv of tetrafluoroboric acid diethyl

ether complex (Sigma-Aldrich) in a dropwise manner, resulting in the precipitation of the tetrafluoroborate salt (*Caution! This reaction is exothermic and easily boils the diethyl ether*). The diethyl ether was removed under vacuum, and the precipitate was washed with two 5 mL portions of diethyl ether. The solid was then dissolved in approximately 3 mL of acetonitrile and reprecipitated by pouring into diethyl ether, followed by decanting the solution and drying the remaining solids under vacuum for approximately 1 h. One recrystallization was sufficient except in the case of 4-nitroanilinium, where two recrystallizations were performed to remove a bright yellow impurity. The same synthetic procedure was followed for the preparation of triethylammonium tetrafluoroborate (initial 1.0 g of Et₃N). **Anilinium:** Yield 1.47 g, 27%. ¹H NMR (CD₃CN, ppm): 7.42–7.53 (multiple peaks, 5H, C₆H₅–), 8.14 (s, 3H, –NH₃). Anal. Calcd: C, 39.83; H, 4.46; N, 7.74. Found: C, 40.08; H, 4.50; N, 7.83%. **4-chloroanilinium:** Yield 0.68 g, 42%. ¹H NMR (CD₃CN, ppm): 7.41–7.54 (multiple peaks, 4H, –C₆H₄–), 8.17 (s, 3H, –NH₃). Anal. Calcd: C, 33.46; H, 3.28; N, 6.50. Found: C, 33.63; H, 3.25; N, 6.55%. **4-*tert*-butylanilinium:** Yield 0.30 g, 20%. ¹H NMR (CD₃CN, ppm): 7.33–7.56 (multiple peaks, 4H, –C₆H₄–), 8.05 (s, 3H, –NH₃), 1.32 (s, 9H, –C(CH₃)₃). Anal. Calcd: C, 50.67; H, 6.80; N, 5.91. Found: C, 50.44; H, 6.67; N, 5.82%. **4-nitroanilinium:** Yield 0.35 g, 23%. ¹H NMR (CD₃CN, ppm): 7.57–8.34 (multiple peaks, 4H, –C₆H₄–), 8.28 (s, 3H, –NH₃). Anal. Calcd: C, 31.90; H, 3.12; N, 12.40. Found: C, 32.07; H, 3.15; N, 12.32%. **4-methoxyanilinium:** Yield 1.06 g, 65%. ¹H NMR (CD₃CN, ppm): 7.05–7.31 (multiple peaks, 4H, –C₆H₄–), 8.01 (s, 3H, –NH₃), 3.79 (s, 3H, –OCH₃). Anal. Calcd: C, 39.85; H, 4.78; N, 6.64. Found: C, 40.03; H, 4.71; N, 6.66%. **4-bromoanilinium:** Yield 0.69 g, 48%. ¹H NMR (CD₃CN, ppm): 7.35–7.69 (multiple peaks, 4H, –C₆H₄–), 8.16 (s, 3H, –NH₃). Anal. Calcd: C, 27.73; H, 2.72; N, 5.39. Found: C, 27.89; H, 2.71; N, 5.37%. **4-cyanoanilinium:** Yield 0.37 g, 22%. ¹H NMR (CD₃CN, ppm): 7.59–7.89 (multiple peaks, 4H, –C₆H₄–), 8.37 (s, 3H, –NH₃). Anal. Calcd: C, 40.82; H, 3.43; N, 13.60. Found: C, 40.65; H, 3.51; N, 13.48. ***N,N*-dimethylanilinium:** Yield 1.10 g, 67%. ¹H NMR (CD₃CN, ppm): 7.41–7.58 (m, 4H, –C₆H₄–), 8.87 (m, 1H, –NHMe₂), 3.24 (s, 6H, –NH(CH₃)₂). Anal. Calcd: C, 45.98; H, 5.79; N, 6.70. Found: C, 45.69; H, 5.82; N, 6.73%. **Triethylammonium tetrafluoroborate:** Yield 1.49 g, 80%. ¹H NMR (CD₃CN, ppm): 6.99 (broad s, 1H, (CH₃CH₂)₃NH⁺), 3.13 (q, 6H, (CH₃CH₂)₃NH⁺), 1.24 (t, 9H, (CH₃CH₂)₃NH⁺). Anal. Calcd: C, 38.13; H, 8.53; N, 7.41. Found: C, 38.33; H, 8.58; N, 7.26%. Full ¹H NMR spectra and peak assignments are given in the Supporting Information.

Electrochemical Methods. Electrochemistry was performed in a nitrogen-filled glovebox with either a Pine Instruments WaveNow or WaveDriver potentiostat using GC working electrodes, a platinum counter electrode, and a silver wire pseudoreference. The WaveNow potentiostat was pumped into the glovebox and connected to an external computer via a custom USB feedthrough, while the WaveDriver potentiostat was kept external to the glovebox, and the electrode leads were connected with a custom shielded electrode cable feedthrough. All scans were absolutely referenced to ferrocene added at the end of each measurement set. GC electrodes [CH Instruments, 3 mm in diameter (used for the majority of experiments); and eDAQ electrodes, 1 mm in diameter and a BASi electrode, 3 mm in diameter, were used for electrode comparison experiments with benzoic acid] were polished with 0.3 μm alumina powder and 0.05 μm alumina powder (CH Instruments, contained no agglomerating agents) Milli-Q water slurries, rinsed, and ultrasonicated for 1 min in high-performance liquid chromatography (HPLC) grade water to remove residual polishing powder. The pseudoreference silver wire electrode was submerged in a glass tube fitted with a porous glass Vycor tip containing 0.1 M [Bu₄N][PF₆] in acetonitrile.

Each working electrode was pretreated with three cyclical scans from approximately 0.7 to –2.8 V (the exact value varied in accordance with the silver wire pseudoreference) at 100 mV/s in 0.1 M [Bu₄N][PF₆]. For all experiments, background voltammograms at the respective scan rate were taken. Following pretreatment and background scans, each electrode was rinsed consecutively in two vials of CH₃CN and air-dried. The solution was stirred between scans. A

potential window was initially established and refined with one working electrode to ensure that the reduction event was captured. For each subsequent scan, the working electrode was replaced with a fresh, pretreated working electrode, and the voltammogram was measured. In the water-dependence experiments, acid was added to yield a concentration of 25 mM, and the potential window of interest was determined with one working electrode. An additional scan was then taken with a fresh working electrode, using the established potential range, for comparison to the water scan. Subsequently, water was added to yield a concentration of 100 mM water, and a voltammogram was recorded with a third working electrode. Unless otherwise noted, current density is based on the *geometric* surface area of the electrode (based on the diameter).

The solution resistance was estimated as detailed in the Supporting Information and used to correct for the ohmic drop for quantitative analyses (e.g., data in Tables 1 and 2, and Figures 5, 8–10). Without

Table 1. Average Acid Reduction Potentials Versus Fc/Fc⁺ in 0.1 M [Bu₄N][PF₆] CH₃CN on GC at 25 mM and 100 mV/s

acid	E_{inf} (V) ^a	notes ^b
water	not obs.	
phenol	-2.60 ± 0.06	
acetic	-2.36 ± 0.05	
triethylammonium	-2.29 ± 0.02	
benzoic	-2.25 ± 0.02	c.c.; pw.
4-cyanoanilinium	-2.06 ± 0.02	
dimethylformamidium	-2.00 ± 0.34	var.
4-methoxyanilinium	-1.95 ± 0.08	pw.; var.
salicylic	-1.94 ± 0.06	
<i>N,N</i> -dimethylanilinium	-1.90 ± 0.06	var.
4-chloroanilinium	-1.86 ± 0.11	var.
anilinium	-1.83 ± 0.07	pw.; var.
4-bromoanilinium	-1.83 ± 0.06	var.
4- <i>tert</i> -butylanilinium	-1.83 ± 0.05	var.
trifluoroacetic	-1.81 ± 0.03	
pyridinium	-1.77 ± 0.09	
<i>p</i> -toluenesulfonic	-1.76 ± 0.15	var.
trichloroacetic	-1.56 ± 0.02	
2-nitrophenol	-1.24 ± 0.02	c.c.
trifluoromethanesulfonic	-1.06 ± 0.02	
4-nitroanilinium	-0.65 ± 0.02	c.c.

^aCVs were ohmic drop corrected prior to E_{inf} determination. Provided value given as the average of three independent measurements, except for dimethylformamidium, for which eight measurements were averaged. Error given as ± one standard deviation. A minimum standard deviation of 0.02 V is given based on the observed drift of the pseudoreference in a half-hour period. ^bAcids displaying curve crossing on the return scan are denoted c.c.; pw. designates acids showing cathodic prewaves, and var. indicates acids that showed significantly different CVs in the same solution with two different GC electrodes.

this ohmic drop correction, the worst case error in reduction potentials was estimated to be approximately 30 mV.

Spectrophotometric Titrations. The pK_a values of 4-chloroanilinium and 4-*tert*-butylanilinium were determined by literature methods in a nitrogen-filled glovebox using dry acetonitrile (see above).¹⁸ Briefly, the extinction coefficients of colorimetric indicators 3-nitroaniline ($pK_a = 7.68^{19}$) and methyl orange ($pK_a = 10.6^{20}$) in the protonated and deprotonated forms were determined by titration with tetrafluoroboric acid diethyl ether complex in acetonitrile. Titration of 3-nitroaniline with 4-chloroanilinium and methyl orange with 4-*tert*-butylanilinium afforded linear plots of [protonated indicator]/[aniline]/[anilinium] versus [indicator], from which the slope was used to calculate the pK_a of the respective anilinium. See Supporting Information for full details and spectra.

RESULTS

Reference Electrode. Two nonaqueous reference electrodes were tested: (1) a reference electrode in which a silver wire was immersed in an acetonitrile solution containing 100 mM [Bu₄N][PF₆] and 10 mM AgNO₃; and (2) a pseudoreference in which a silver wire was immersed in an acetonitrile solution containing 100 mM [Bu₄N][PF₆]. In both cases the silver wire and electrolyte solution were contained in a glass tube fitted with a porous Vycor glass frit. Ferrocene was added at the end of each measurement set as an absolute reference. Reference electrode 1 was observed to occasionally contaminate the bulk solution with silver ions, as suggested by an oxidation at approximately -0.24 V versus Fc/Fc⁺. By comparison to pure silver nitrate, the contamination proved to be the stripping of reduced silver off the GC electrode (Supporting Information, Figure S7). This contamination of the bulk solution with silver ions was observed to result in variable reduction potentials for some acids. Silver is likely a better catalyst for hydrogen evolution than GC; as such, any silver contamination may shift the acid reduction potential more positive.

A Ag/AgCl pseudoreference immersed in an acetonitrile electrolyte solution in a glass tube equipped with a porous Vycor frit was not used because silver chloride is somewhat soluble in acetonitrile (especially if solution chloride anions are present),²¹ and we wished to avoid the possibility of solution contamination by silver ions. Consequently, pseudoreference electrode 2 was chosen for acid reduction measurements. Over a 30 min period the pseudoreference electrode was observed to drift 15 ± 14 mV by monitoring the $E_{1/2}$ position of the ferrocene/ferrocenium couple (0.8 to 1.8 mM ferrocene) in a 100 mM [Bu₄N][PF₆] acetonitrile solution. While extensive studies were not done, the solute may influence drift rate.

Electrode Fouling. Significant variability between sequential CVs was observed if the GC working electrodes were not polished prior to each scan. Pyridinium chloride was the clearest example (Figure 2a). Upon subsequent scans the current density greatly decreased. It was difficult to observe the ferrocene/ferrocenium wave after these scans. Visual examination of the GC electrode post measurement revealed that the surface was coated in a mirror-like yellow film. Figure 2b,c shows the positive and negative shifts of the reduction current for subsequent scans of trifluoroacetic and acetic acid, respectively. Such variability was minimized for most acids when only fresh electrode surfaces were used (see below for exceptions).

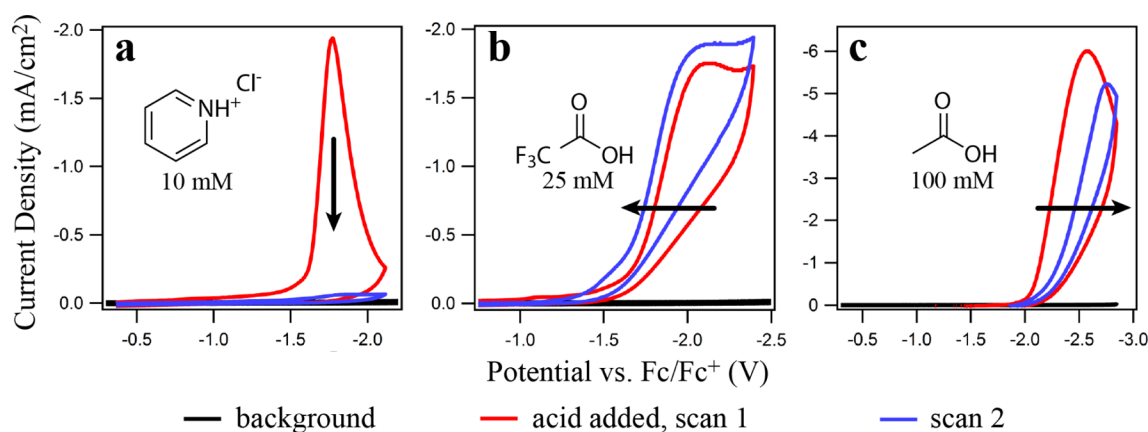
Acid Reduction Measurements. To avoid electrode fouling, freshly polished and electrochemically pretreated GC electrodes were used for each CV. In a typical experiment, a number of GC electrodes were polished in alumina/water slurries, ultrasonicated, and rinsed with acetone before being brought into a nitrogen-filled glovebox. Prior to adding acid, each GC electrode was electrochemically pretreated (by cyclically scanning between approximately 0.7 and -2.8 V at 100 mV/s three times in 100 mM [Bu₄N][PF₆] solution), and a background scan recorded in the 100 mM [Bu₄N][PF₆] acetonitrile solution.

It was checked if the GC electrode surface changed over time after pretreatment. After pretreatment, a background scan was taken, and the electrode was rinsed in acetonitrile. It was then left under nitrogen for 2 h before the acquisition of a second background scan. Little difference was observed between the two scans (Supporting Information, Figure S8).

Table 2. pK_a and Homoconjugation Values in CH_3CN for Acids Studied in This Work and Influence of 100 mM Water on the Reduction Wave Peak Current

acid	pK_a in CH_3CN	ref. ^a	$\log(K_f)$ (species) ^b	current increase with water? ^c
perchloric ^d	1.57	24		n/a
hydronium ^d	2.2	25	3.9 (B_2H^+), 4.7 (B_3H^+), 5.3 (B_4H^+)	n/a
trifluoromethanesulfonic ^e	2.6	24		yes
dimethylformamidium	6.1	26		~
4-nitroanilinium	6.22	19		no
4-cyanoanilinium	7	27	≤ 0.6 (estimated) ^f	no
<i>p</i> -toluenesulfonic ^g	8.6	28	3.0 (HA_2^-)	~
4-bromoanilinium	9.43	19		~
4-chloroanilinium	9.7	a		~
anilinium	10.62	19	0.6 (B_2H^+)	~
trichloroacetic	10.75	24	2.5 (HA_2^-)	no
4- <i>tert</i> -butylanilinium	11.1	a		~
<i>N,N</i> -dimethylanilinium	11.43	19		~
4-methoxyanilinium	11.86	19		~
pyridinium	12.53	19	0.8 (B_2H^+)	no
trifluoroacetic	12.65	24	3.9 (HA_2^-)	yes
salicylic ^h	16.7	24	3.3 (HA_2^-)	yes
triethylammonium	18.82	19	~ 0 (B_2H^+)	yes
benzoic	21.51	28	3.6 (HA_2^-)	no
2-nitrophenol	22.85	28	2.0–2.2 (HA_2^-) ⁱ	no
acetic	23.51	28	3.9 (HA_2^-)	yes
phenol	29.14	29	4.2 (HA_2^-), 5.7 (H_2A_2^-)	yes
acetonitrile ^d	≥ 32.2	30		n/a
water ^d	38–41 ^j	31		n/a

^aFor pK_a values determined in this work an "a" is given. All other pK_a values taken from the references indicated. ^b K_f is the homoconjugation formation constant. The species formed is shown in parentheses; data taken from ref 24, where the most recent values were used. Reference 28 lists alternative homoconjugation for acetic acid (4.5) and benzoic acid (3.9); however, it was not clear how these values were obtained. Species with neutral conjugate bases are designated B, while species with anionic conjugate bases are denoted A. All K_f values were rounded to one decimal place. Hyphens indicate that no data were found. ^cFor the acids which showed irreproducible CVs a ~ is shown instead. For acids that were not measured, n/a (not applicable) is written. ^dData on perchloric acid, hydronium, acetonitrile, and water are included for reference. ^eThe pK_a of trifluoromethanesulfonic acid was measured as 2.6 (ref 24) and recently estimated as 0.7 (ref 32). We note that the direct reaction of acetonitrile with trifluoromethanesulfonic acid (see Electrode and Solvent Fouling section and ref 33) render these pK_a values suspect. ^fThe homoconjugation constant of 4-cyanoanilinium was estimated as being less than that of anilinium in ref 17. ^gWe utilized the monohydrate form; it is unclear what form this acid was in for the listed pK_a . ^hSalicylic acid is also reported to form a (2HA) complex with a pK_a of 13.6.²⁴ ⁱSee ref 28 for compilation of homoconjugation values of 2-nitrophenol. ^jEstimated values from ref 31. It has been noted that pK_a values that are greater than the autoprotolysis constant of acetonitrile may have no physical meaning (ref 31).

**Figure 2.** Cyclic voltammograms of three acids in acetonitrile using a GC electrode showing the response of the electrode on subsequent scans. Scan rate = 100 mV/s, 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$.

Twenty acids over an approximately 26 pK_a unit range plus water were selected for measurement. The reduction wave of each acid at 25 mM was independently measured three times at 100 mV/s. Representative CVs of each acid at 25 mM for both 100 and 1000 mV/s scan rates are recorded in the Supporting Information (Figures S9–S50). Comparison of

the 100 and 1000 mV/s scans revealed that the current response usually did not peak in the 1000 mV/s scan as compared to the clear maximums observed at the 100 mV/s scan rate. While detailed electrochemical measurements of these acids was not the goal of this work, below are general observations.

For two acids—benzoic acid and 4-nitroanilinium—the return sweep cathodically crossed the forward sweep. For benzoic acid this curve crossing was more pronounced at higher concentrations (Supporting Information, Figure S51) and less distinct at faster scan rates (Supporting Information, Figure S52). 4-nitroanilinium also displayed curve crossing; however, at higher scan rates the crossing did not appear to decrease (Supporting Information, Figure S53).

Anilinium, benzoic acid, 4-methoxyanilinium, and 4-cyanoanilinium reproducibly showed cathodic current peaks preceding the main reduction. Figure 3 shows the current

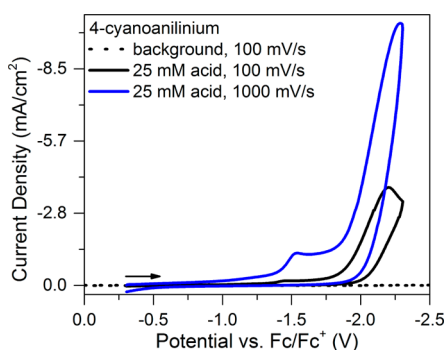


Figure 3. Cyclic voltammograms of 25 mM 4-cyanoanilinium (100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solution) at 100 and 1000 mV/s showing the presence of a prewave on the forward sweep.

response of 4-cyanoanilinium at 100 and 1000 mV/s—at 1000 mV/s the prewave increased proportionally more relative to the main reduction. Upon repeating the 100 mV/s scan, without polishing, the prewave vanished. No prewave is seen in a literature example for a solution of 10 mM 4-cyanoanilinium,²² suggesting the presence of prewaves may highly depend on small variations of the GC electrode surface. However, a concentration dependence study of 4-cyanoanilinium revealed a lack of a prewave at 5 and 10 mM but an appearance of the prewave at 25 mM (Supporting Information, Figure S86).

For every acid, measurements at 100 mV/s and 25 mM were made with two separate GC electrodes and compared. In most cases the only noticeable difference was variation in peak currents; however, seven of the acids containing aromatic groups—4-bromoanilinium, 4-chloroanilinium, 4-*tert*-butylanilinium, anilinium, *N,N*-dimethylanilinium, 4-methoxyanilinium, and *p*-toluenesulfonic acid monohydrate—showed substantially dissimilar CVs taken immediately after one another using only freshly prepared GC electrodes. Figure 4 shows one representative example for 4-chloroanilinium where the wave shape and wave position changed dramatically. To check whether or not this acid was particularly sensitive to changing electrode surfaces, both electrodes were removed, repolished, and re-pretreated. Acquisitions of two new scans in the same solution, also shown in Figure 4, revealed that while neither scan resembled the prior scans in location or peak current, both traced each other very closely. Subsequent experiments continued to yield highly variable wave shapes and positions but failed to give identical results to those shown in Figure 4. ¹H NMR analysis of aliquots of the 4-chloroanilinium solution prior to any measurements and after measurements revealed no differences in the bulk solution—the only observed peaks were of 4-chloroanilinium, $[\text{Bu}_4\text{N}][\text{PF}_6]$, and acetonitrile.

Reduction Potentials. As shown in Figure 5, reduction values were calculated by taking the derivative of the forward

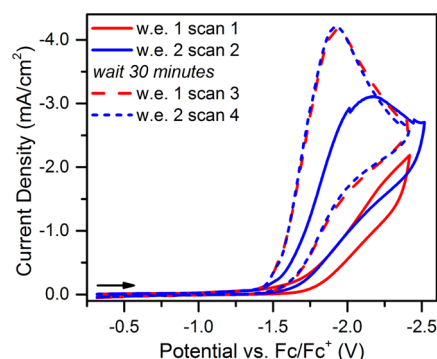


Figure 4. Cyclic voltammograms (100 mV/s) of 25 mM 4-chloroanilinium in a 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solution using two different GC working electrodes (w.e. 1 and w.e. 2). Scan number indicates the total number of scans taken.

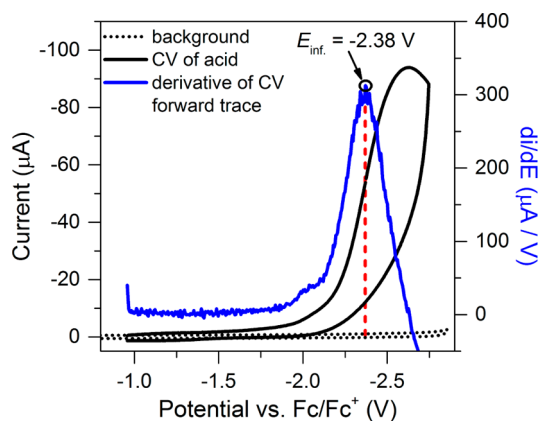


Figure 5. Cyclic voltammogram of 25 mM acetic acid at 100 mV/s in 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solution and the first derivative of the forward trace. The dashed vertical line denotes the inflection point potential.

scan for each acid at 25 mM and identifying the maximum of this derivative as the irreversible reduction potential inflection point, E_{inf} .

Table 1 summarizes the inflection reduction potential E_{inf} for each acid studied as the average of three independent scans measured at 100 mV/s. Values of E_{inf} for the various acids spanned most of the cathodic solvent window, ranging from -0.65 to -2.60 V versus Fc/Fc^+ . While the standard deviation was typically on the order of tens of millivolts, 4-chloroanilinium, dimethylformamidium, and *p*-toluenesulfonic acid showed greater than 100 mV standard deviation. Dimethylformamidium was particularly inconsistent—measurements taken within a few hours with identical solvent and material sources yielded values differing by over 600 mV. At room temperature, ¹H NMR dimethylformamidium was not observed to react with deuterated acetonitrile. Table 1 also details which acids were found to be variable (e.g., yield irreproducible CVs scan to scan; see Figure 4 and associated discussion above), show curve crossing on the return scan, or to have a distinct prewave.

Since the surface chemistry, and hence electrochemical response, of GC is complex,²³ it was checked whether electrodes from another supplier could yield different E_{inf} values. Consequently, in addition to the E_{inf} value reported in Table 1 for benzoic acid found using CHI electrodes (3 mm in diameter), benzoic acid was also analyzed with electrodes from two other suppliers (eDAQ, 1 mm in diameter GC electrode

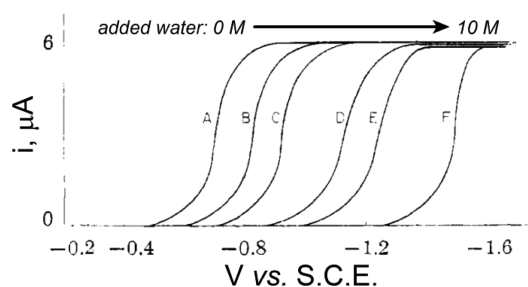


Figure 6. Polarography of 1 mM perchloric acid on a dropping mercury electrode with added water in acetonitrile (A, B, C, D, E, F: 0, 0.01, 0.1, 1.0, 3.0, and 10 M added water). Adapted with permission from ref 13.

that exceed the autoprotolysis constant of acetonitrile may be meaningless.³¹ For weaker acids, water can have the opposite effect, stabilizing the dissociation products and so increasing acid strength.⁴⁶

Homoconjugation. Because of the weak cation and even weaker anion solvating ability of acetonitrile, dissociated species can gain additional stability by forming homoconjugated complexes with the parent compound.^{35,47} In the prototypical example, acid HA dissociates in solvent S to form solvated H⁺ (by solvent or HA) and A⁻, followed by association of A⁻ with HA to form the hydrogen-bonded homoconjugation complex [A⋯HA]⁻.



Homoconjugation can consequently increase the apparent acidity of the parent acid by displacing the equilibrium toward deprotonation at the expense of reducing the overall concentration of free HA.

As homoconjugation can complicate electrochemical studies of hydrogen-evolving catalysts and result in multiple catalytic cyclic voltammetric waves,¹⁷ it is desirable to know at which concentrations homoconjugation is less influential. It is not feasible to generally comment at which concentrations homoconjugation becomes less appreciable for all acids, but a value of 0.001 N (0.001 M effective acidic proton concentration) was proposed.²⁶ A parameter κ was recently suggested to provide a more specific estimate for the extent of homoconjugation:¹⁷

$$\kappa = K_f C_0 \quad (5)$$

where C_0 is the total acid concentration and K_f is the formation constant of the homoconjugation complex:

$$K_f = \frac{[[\text{A}\cdots\text{HA}]^-]}{[\text{A}^-][\text{HA}]} \quad (6)$$

For $\kappa \gg 1$, the acid completely homoconjugates; for $\kappa \ll 1$, the acid does not appreciably homoconjugate. For example, an acid with $\log(K_f) = 2.0$ ($K_f = 100$) has a κ equal to 10 when $[\text{acid}]_{\text{total}} = 0.1$ M. As most catalytic studies use acid concentrations between 0.01 and 1 M, homoconjugation is almost certainly always occurring in measurements that utilize homoconjugating acids.

Homoconjugation is expected to influence acid electroreduction. If the acid is reduced to hydrogen, an equivalent of the conjugate base is formed, and the concentration of conjugate base will rapidly increase near the electrode surface, engaging in homoconjugation reactions with the parent acid if

favorable and so perturbing the K_f equilibrium. These homoconjugates ($[\text{A}\cdots\text{HA}]^-$) may have reduction potentials different than the parent acid. Along those lines of logic, homoconjugation has been suggested to produce multiple catalytic reduction waves for hydrogen-evolving catalysts.¹⁷ Artero et al. have suggested that complications arising from homoconjugation can be successfully accounted for theoretically on an acid-by-acid basis.¹⁷

Preferably, acids should be chosen with small, or preferably nonexistent, homoconjugation properties. For example, 2-nitrophenol has very weak (or nonexistent) homoconjugation tendencies because the ortho-positioned nitro group stabilizes the neutral, undissociated phenol proton by intramolecular hydrogen bonding preferentially over hydrogen bonding with dissociated 2-nitrophenoxide.^{28,41} However, as detailed below, 2-nitrophenol is unsuitable for hydrogen-evolution catalysis because of its very positive reduction potential. Cationic acids, which form neutral conjugate bases, may also be expected to form homoconjugated complexes more weakly, as cationic and especially neutral species are generally more easily solvated by acetonitrile than anionic species. Table 2 displays the $\log(K_f)$ values of three cationic acids—anilinium, pyridinium, and triethylammonium. The $\log(K_f)$ values are all less than 1, such that $\kappa = 10$ is only obtainable with 1–10 M acid.

If acids that homoconjugate must be used, the complications arising from homoconjugation can be reduced by using 1:1 mixtures of acid and the conjugate base.⁴⁸ Under the condition of pseudo-first-order catalysis (no meaningful change in substrate concentration near the electrode) the amount of A⁻ produced by deprotonation of HA will drive the equilibrium of eq 3 to the right, increasing the contribution of homoconjugation over the time scale of the experiment. By using 1:1 mixtures of acid and conjugate base, the amount of A⁻ produced during catalysis will not meaningfully change the concentration of A⁻ already present. Hence, the extent of homoconjugation will be approximately the same throughout the measurement, rather than increasing in importance in the case where no conjugate base is initially present.

If acids that do not homoconjugate appreciably must be employed, then 50/50 mixtures of acid/conjugate base should be used to reduce changes on the experimental time scale and/or the theoretical methods developed by Artero et al. to correctly account for homoconjugation used.¹⁷

Electrode and Solvent Fouling. While it is established that GC electrodes readily adsorb solvent impurities and become easily fouled by analytes,^{23,49} this fact is rarely discussed in the nonaqueous electrochemical hydrogen-evolution community. Figure 2 graphically demonstrates that even using an electrode only twice without polishing can yield inconsistent CVs. Most dramatic was the case of pyridinium, which appeared to form an insulating film after one reductive scan. This has precedent: reduction of quaternary pyridiniums in water resulted in film deposition on GC,⁵⁰ and quaternary pyridiniums were also reported to adsorb readily onto platinum electrodes, forming an insulating layer.⁵¹ Additionally, preliminary studies in our group, using a variety of homogeneous catalysts for hydrogen evolution, have yielded irreproducible CVs when the same working electrode was used for multiple scans without polishing, strongly suggesting that the electrode surface can be noticeably altered scan to scan. Surface modification can even involve deposition of heterogeneous particles, which can independently evolve hydrogen.⁵² As shown in Figure 7, using only freshly prepared electrode surfaces resulted

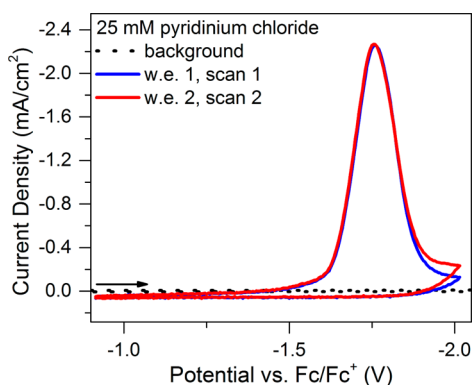


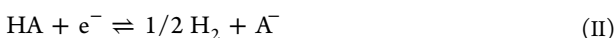
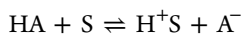
Figure 7. Cyclic voltammograms of 25 mM pyridinium chloride in 100 mM $[\text{Bu}_4\text{N}][\text{PF}_6]$ acetonitrile solution at 100 mV/s showing reproducibility if only freshly polished working electrodes are used. Here, two working electrodes, namely, w.e. 1 and w.e. 2, were used.

in reproducible scans. Accordingly, reiterated here, GC working electrodes—whether used for acid reduction or catalytic studies—should be polished between every scan. Even with only freshly polished electrodes the possibility exists that fouling occurring during a single scan will influence the recorded voltammogram.

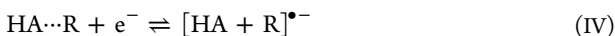
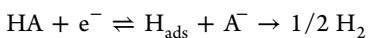
Apart from electrode fouling, the bulk solvent composition itself can change. While little information is available on the interactions of common acids with acetonitrile, trifluoromethanesulfonic acid reacts with acetonitrile, forming a multitude of products.³³ At higher ratios of trifluoromethanesulfonic acid to acetonitrile (14:1 and 2:1), over 10 species were formed. At lower ratios (1:200), only acetamide was seen. Note that for the 1:200 experiment the mixture of acetonitrile and trifluoromethanesulfonic acid were boiled in CD_2Cl_2 prior to spectral acquisition. We independently confirmed that trifluoromethanesulfonic acid reacts with acetonitrile at room temperature by ^1H NMR (Supporting Information, Figure S84).

These unknown degradation products could interact with a catalyst in unanticipated ways—including degrading the catalyst. It is crucial that acids be checked for possible direct interactions with the solvent and catalyst prior to reduction. Of the acids studied here, only trifluoromethanesulfonic acid is known to interact with acetonitrile, and it is anticipated that the weaker acids, incapable of protonating acetonitrile, will be relatively unreactive.

Acid Reduction. Four possible categories for acid (HA) reduction at an electrode in solvent S have been proposed;⁵ note that acid reduction does not necessarily stipulate the formation of H_2 :



or on certain metal electrodes:

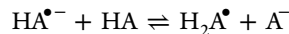


Category I acids are strong acids that dissociate to form solvated protons and conjugate base prior to the reduction of solvated protons to form hydrogen. Of the acids studied here,

only trifluoromethanesulfonic acid approaches pure Category I in strength and as noted above reacts directly with acetonitrile. Category II acids are not strong enough to be dissociated, so hydrogen evolution occurs via direct acid reduction. In the case of a platinum electrode, the hydrogen evolution process occurs through downstream processes of electrode-adsorbed hydrogen atoms—for example, interaction of a surface-bound hydrogen atom with a solution proton and an additional electron.⁹ Variations of this process, such as coupling of two H_{ads} , occur for other metal electrodes.⁹

It is unclear how Category II processes would occur on GC, but possible hydrogen atom adsorption or a bimolecular process involving two acid molecules may be envisioned. GC possesses surface oxygen-containing sites, including carboxylic acid and alcohol functionalities⁴⁹ that may serve as surface “docking sites” for protons prior to final reduction to hydrogen.

Category III acids have a sufficiently low-lying lowest unoccupied molecular orbital such that direct hydrogen evolution (i.e., via a Category II route) is preceded at more positive potentials by the formation of a radical species. Finally, Category IV describes the scenario where reduction results in release of an atom or group from the host acid. This category is a unique subset of Category III acids in which reduction is followed by fragmentation of the acid. Alternatively, acid radicals can undergo further chemistry with the parent acid through self-protonation reactions^{53–55}



The four proposed acid reduction pathways were based on experiments done in organic solvents with platinum working electrodes. Reduction of acids in acetonitrile with GC working electrodes is distinctive in that GC is often cited as a “non-catalytic” surface for hydrogen evolution.^{5,6,10} With hydrogen evolution requiring more driving force on GC, alternative reduction pathways necessitating less driving force, such as those forming radicals, may out-compete hydrogen evolution. As product distribution measurements were not undertaken here, it is unclear whether the acids in this study are reduced to evolve hydrogen (Category II) or radical anions (Categories III and IV).

Acids used for catalytic hydrogen-evolution studies are usually assumed to only donate protons to the catalyst. While it may be more likely that the reduced catalyst accepts protons from the acid to form hydrogen, solution electron transfer from the catalyst to the acid—forming radical acid species—should also be possible. The resulting cyclic voltammograms would likely be very similar to those for catalytic hydrogen evolution and could easily be misinterpreted as catalytic hydrogen evolution. Further analysis that confirms hydrogen as the dominant or sole product (e.g., by gas chromatography) is therefore necessary. As most literature catalysts are reported along with gas chromatography measurements of produced hydrogen, it seems that this alternative pathway of catalytic solution electron transfer to reduce the acid is either very uncommon or underreported.

Insight into the reduction pathways of some acids studied here may be gleaned. A significant subset of the aromatic acids yielded highly variable CVs in the same solution using different, freshly prepared electrodes. In the case of 4-chloroanilinium, a secondary experiment was performed to evaluate possible differences between different electrodes. The solution was initially scanned with two different electrodes, both of which were removed, repolished, re-pretreated in blank electrolyte,

and then used to measure CVs in the original 4-chloroanilinium solution. While the first two scans did not match (Figure 4), the second set was very similar, suggesting that the bulk solution composition had changed since the first measurement. A change in the bulk composition is not consistent with any one CV experiment, however, as only a small amount of acid near the electrode surface is reduced.

If reduction were occurring by a radical pathway, however, the first measurement could initiate bulk solution radical chemistry. The second measurement would have probed the solution as it began changing, and by the time the two electrodes had been repolished and re-pretreated, this chemistry had yielded a new bulk composition. However, this time course analysis of 4-chloroanilinium was not reproducible—while the wave shapes, positions, and peak currents were clearly different from scan to scan, there was no consistent trend when comparing separate experiments. ¹H NMR analysis of dried samples of the solution before and after electrochemistry revealed no differences, suggesting that bulk solution radical chemistry did not occur.

While no bulk solution radical chemistry was observed, reduction to form radicals near the electrode—where chemistry on the time scale of a single cyclic voltammogram could result in variable near-electrode solution compositions scan to scan—could still explain the irreproducible nature of some of the acids. The possibility that aromatic compounds can be reduced to radicals followed by further reduction and/or decomposition is the subject of textbook explanations of various electrochemical mechanisms.⁵⁶ It was not within the scope of this work to further experimentally investigate the possible formation of radicals, although we note that reduction to radical species is the likely pathway of some of the reported acids.

Reduction Potentials. The reduction potentials of 20 acids at 25 mM and 100 mV/s in 0.1 M [Bu₄N][PF₆] acetonitrile solutions are reported in Table 1 (additional cyclic voltammograms at 1000 mV/s are included in the Supporting Information). No reduction was observed for water. For no acid was the reduction observed to be reversible, unlike the reversible or quasi-reversible nature of acid reduction seen on platinum electrodes.^{10,57} Note that the reported values may show a small dependence on electrolyte identity.

Because of the lack of reversibility, no thermodynamically precise reduction values could be assigned.¹³ However, it was still desirable to report reduction potential for the acids studied for comparative purposes. Reduction values were obtained by finding the maximum of the derivative of the forward scan—the inflection point, E_{inf} . A similar method was proposed as a way to estimate the midwave potential for catalytic CVs,¹⁷ although it should be noted that the theory used in that work is not translatable to the strictly irreversible processes seen here. Alternative methods were considered, including (a) taking the potential at maximum peak current, (b) the potential at half peak current, and (c) defining a threshold current density as the “onset” potential. Peaks were not always observed, especially at higher scan rates where depletion of the acid did not occur quickly enough to result in a peak in the potential window studied. The loss of peak shape at higher scan rates is clearly illustrated for acetic acid, which was measured up to 9000 mV/s (Supporting Information, Figure S85). Methods (a) and (b) were consequently not chosen, and method (c), setting a threshold current density, is inherently arbitrary.¹⁷ The E_{inf} method was chosen here for practicality. Note also that while taking the derivative of a reversible cyclic voltammogram is

equivalent to a differential pulse voltammogram of the same system, this is not the case for an irreversible process. For an irreversible process equilibrium is not maintained during the forward/backward potential steps of differential pulse voltammetry, resulting in a different current response.

Using pK_a values either taken from the literature or determined in the present study, E_{inf} values for each acid were plotted against the appropriate pK_a (Figure 8). Figure 8 also

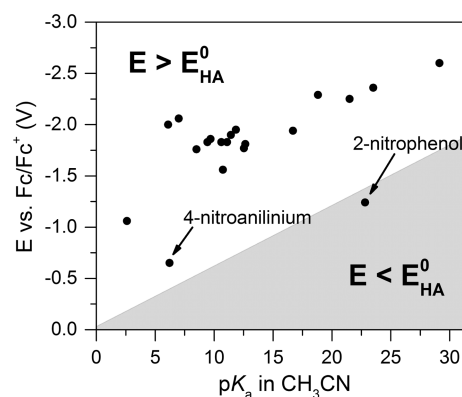


Figure 8. Plot of E_{inf} values vs the respective pK_a value for each acid studied. The gray region is an estimation of the zone in which the applied potential is thermodynamically insufficient to reduce acids to hydrogen ($2\text{HA} + 2e^- \rightleftharpoons \text{H}_2 + 2\text{A}^-$). See text for details.

includes a gray region that indicates where it is thermodynamically impossible to reduce an acid to hydrogen and its conjugate base. The boundary of this zone was calculated using eq 7:⁸

$$E_{\text{HA}}^0 = E_{\text{H}^+/\text{H}_2}^0 - (2.303RT/F) \cdot pK_a(\text{HA}) \quad (7)$$

where -0.028 V (vs Fc/Fc⁺) was used as the value of $E_{\text{H}^+/\text{H}_2}^0$.¹⁷ See ref 17 for a recent discussion of $E_{\text{H}^+/\text{H}_2}^0$ values.

A linear trend is observed between E_{inf} values for each acid and the respective pK_a (Figure 8), with weaker acids having more negative E_{inf} values. This is consistent with linear trends seen in dimethyl sulfoxide^{6,58} and with gas-phase measurements,⁵⁹ supporting the thermodynamic suggestion that weaker acids require more driving force to yield hydrogen (see Discussion section above). 4-nitroanilinium lies relatively close to the thermodynamic boundary as compared to the main group of acids, and 2-nitrophenol occurs within the zone where hydrogen evolution should be thermodynamically prohibited. Deviation from the linearity of reduction potential versus pK_a has been observed for nitro- and cyano-substituted methylanthracenes, derivatives in which the possibility of resonance interactions between the nitro/cyano group and the aromatic system were cited as possible explanation.⁵⁸ Similar resonance interactions likely apply here, possibly encouraging direct reduction to radical species, which would have different thermodynamic requirements. Alternative reduction pathways involving formation of radical species are suggested to account for the deviation from linearity of some of the anilinium compounds (see Acid Reduction section above).

The potential at which it is thermodynamically possible to reduce an acidic proton with known pK_a was estimated using eq 7 with -0.028 V as the value for $E_{\text{H}^+/\text{H}_2}^0$.¹⁷ The usefulness of eq 7 has been questioned¹⁷ as it does not account for multiple phenomena, including homoconjugation, which significantly affects most acids in acetonitrile at the concentrations usually

employed. Consequently, the thermodynamic region depicted in Figure 8 is oversimplified, as these values should be acid- and concentration-dependent. The thermodynamics of acid reduction to hydrogen continues to be discussed,^{16,17,48} and further comment here is not the intended goal of this work.

The E_{inf} values in Table 1 do not accurately convey the amount of background current passed at potentials prior to E_{inf} , especially for acids that exhibited prewaves (Figure 3, see Table 1). Prewaves can be explained by adsorption of the reduced product where the adsorption free energy reduces the energy—and thus the applied potential—needed for reduction.⁵⁰ To more accurately capture the presence of background current like prewaves, an alternative method of presenting the background current passed between the minimum thermodynamic potential E_{HA}^0 and E_{inf} is shown in Figure 9. Here, the

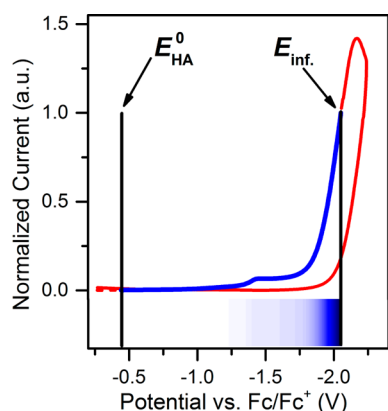


Figure 9. Background-subtracted cyclic voltammogram of 25 mM 4-cyanoanilinium at 100 mV/s, normalized to the current measured at E_{inf} . The color scale was mapped onto the normalized current values, where white indicates no current being passed above the background current, and dark blue indicates the level of current passed at the inflection point.

current has been background-subtracted and normalized relative to the current passed at E_{inf} . A color gradient was subsequently mapped onto the normalized current versus potential values.

The color scale in Figure 9 of 4-cyanoanilinium reflects what the E_{inf} value does not: the presence of a prewave prior to the main reduction event. Using this method, a mapped gradient color scale was generated for each acid studied (Figure 10), and acids were categorized into three categories: (a) eight recommended acids that showed reproducible backgrounds, (b) eight acids with erratic backgrounds, and (c) four acids we suggest as unsuitable for electrochemical hydrogen-evolution studies in acetonitrile.

Figure 10 captures the presence of prewaves or other significant nonbackground current being passed prior to the E_{inf} value, and so highlights the fact that certain acids (e.g., *p*-toluenesulfonic acid) pass some current above background over most of the potential range while other acids (e.g., pyridinium) pass relatively little current prior to the main reduction wave. It is hoped that Figure 10 can be used to rapidly choose candidate acids such that (a) the acid can be thermodynamically reduced to hydrogen at the relevant redox potential of a given catalyst and (b) that direct electrode acid reduction is avoided.

Influence of Water. Cyclic voltammograms were recorded for each acid with and without 100 mM added water. For six acids—acetic acid, *p*-toluenesulfonic acid monohydrate,

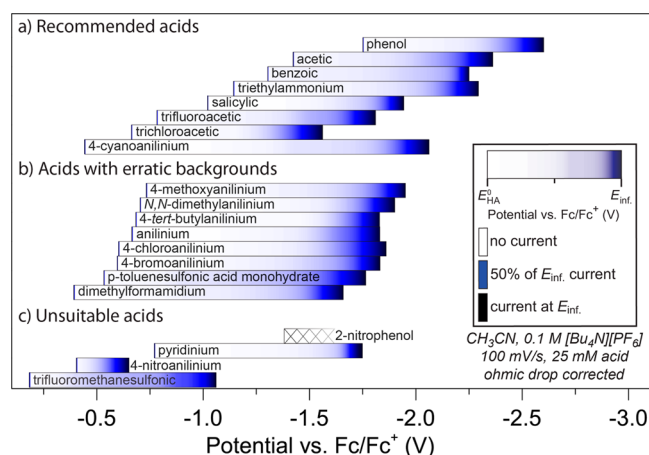
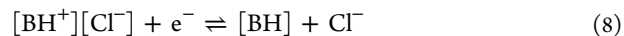


Figure 10. Acid potential windows in acetonitrile (25 mM acid, 100 mV/s) showing the range between an approximate thermodynamic potential E_{HA}^0 (where proton reduction to hydrogen is thermodynamically possible) and the direct reduction potential E_{inf} . The color scale was constructed by choosing a representative CV with an E_{inf} close to the average E_{inf} value and normalizing between 0 (background current without acid, white) and 1 (current at E_{inf} , dark blue). Data more positive than the thermodynamic reduction potential E_{HA}^0 (based on eq 7) was then removed. Prewaves and significant current prior to E_{inf} are visible for some acids. Unsuitable acids: (1) the E_{inf} value of 2-nitrophenol was more positive than the E_{HA}^0 for 2-nitrophenol, (2) pyridinium upon reduction was observed to passivate the electrode, which may occur accidentally during catalysis without strictly avoiding any direct reduction, (3) 4-nitroanilinium has a very limited potential range and so was judged unsuitable, (4) trifluoromethanesulfonic acid can react directly with acetonitrile; see main text.

triethylammonium, trifluoroacetic acid, phenol, and trifluoromethanesulfonic acid—the peak current density increased (see Supporting Information for all CVs). Five of these acids have anionic conjugate bases, and so it would be expected that upon reduction each equivalent of conjugate base would homoconjugate with the parent acid, limiting the amount available for reduction. Water could stabilize these anionic conjugate bases (heteroconjugation), freeing additional acid for reduction and resulting in enhanced peak current.^{28,46} Why then did triethylammonium, which forms a neutral conjugate base and homoconjugates comparatively weakly (Table 2), show a current increase? A possible explanation involves the chloride counteranion. Reduction results in release of chloride:



In the absence of water, chloride released after reduction may obtain stability by homoconjugating with the parent acid, again decreasing the amount of parent acid available for reduction. Water is expected to preferentially solvate chloride and consequently free additional acid for reduction, resulting in increased current. It is possible that less or no current increase would be seen for a triethylammonium species with a softer counteranion, and indeed a sample of triethylammonium tetrafluoroborate showed no current increase upon addition of 100 mM water (Supporting Information, Figure S89).

However, these explanations are insufficient. Specifically, why did the current dramatically increase for acetic and trifluoroacetic acid but not trichloroacetic acid? The stabilizing influence of water is clearly more subtle and warrants further investigation.

The key question originally posed was to determine whether water shifted the reduction potential as observed for perchloric

acid. For weak acids it has been noted that water can stabilize the dissociated products and so increase the apparent acidity.^{28,46} As stronger acids are thermodynamically easier to reduce, it was hypothesized that the addition of water might result in a positive shift in reduction potential and thus potentially interfere with catalysis.

While slight shifts in reduction potential were observed upon addition of 100 mM water for some acids (see Supporting Information for all CVs), in no case did the E_{inf} values for added water fall outside $E_{\text{inf}} \pm 1 \sigma$ when no water was present. While more significant potential shifts were observed for some acids, these same acids exhibited variability scan to scan (see Table 1); hence, we could not trust the potential shifts. Unlike perchloric acid, all of the acids studied here are much weaker acids, and so proton transfer to water to form hydronium is not expected to occur to any great extent. Since the addition of water did not appear to significantly shift E_{inf} for any acid studied, the current enhancements seen for some literature catalysts when small amounts of water are added are unlikely due to direct acid reduction current shifting anodically and overlapping with the catalytic current. An alternative explanation is that the increased acidity of acids in acetonitrile with water present^{28,46} results in faster catalytic rates as a result of the increased driving force for deprotonation; however, our data indicate any change in $\text{p}K_{\text{a}}$ with 100 mM added water does not strongly influence the reduction potential at GC. While larger concentrations of water were not studied, at some ratio of acetonitrile/water the acid $\text{p}K_{\text{a}}$ values will change enough to effect a clear change in the reduction potential. This critical ratio is expected to be unique for each acid, and further study is welcomed. Lastly, we note that current enhancement for electrocatalysts upon water addition has also been attributed to water's ability to act as a proton relay capable of more readily accessing the sterically crowded metal sites as compared to the parent acid.¹¹

CONCLUSION

The electroreduction of 20 acids plus water on GC in acetonitrile was investigated. Figure 10 presents the approximate potential windows in which acids may be used for catalytic hydrogen evolution while (a) avoiding direct reduction and (b) allowing for the thermodynamic possibility of reduction to hydrogen. Figure 10 additionally includes our recommendations for which acids to use, which acids give problematic backgrounds, and which acids are generally unsuitable for hydrogen-evolution catalysis in acetonitrile. We reiterate that accurately determining the thermodynamic potential is more complex^{16,17,48} than what was considered here.

Although the proper acid selection should minimize interference, backgrounds of respective acid reduction at the correct concentration and scan rate should always be provided alongside catalytic cyclic voltammograms. This work is not intended to replace independent acid-only measurements—especially as only one concentration and scan rate were thoroughly investigated for each acid here. While alternative electrodes were not tested, it has been noted that mercury-coated gold electrodes can shift direct acid reduction potentials more negative, providing a larger working potential window.⁸ The importance of polishing the working electrode before every measurement, while perhaps assumed by most researchers, is also underscored. The addition of 100 mM water was not found to clearly shift the reduction potential at GC for any acid

studied, although current enhancement was observed for some acids when water was added.

ASSOCIATED CONTENT

Supporting Information

UV-vis spectra and details on spectrophotometric $\text{p}K_{\text{a}}$ determination, cyclic voltammograms including representative plots for all acids, and ^1H NMR spectra of reported compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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