Supporting Information

Reactivity of Proton Sources with a Nickel Hydride Complex in Acetonitrile: Implications for the Study of Fuel-Forming Catalysts

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SI–1 Determination of acid $pK_a$ for previously unknown acids

$4$-methylanilinium tetrafluoroborate

![NMR spectrum](image)

**Figure S1.** $^1$H NMR of $4$-methylanilinium tetrafluoroborate in CD$_3$CN.

The $pK_a$ of $4$-methylanilinium in acetonitrile was determined via spectrophotometric titration as previously described.$^1$ $4$-methylanilinium was titrated into a solution of methyl orange (MO, $pK_a = 10.6$) and the protonated methyl orange (MOH$^+$) absorbance was monitored by UV-vis absorbance spectroscopy at $\lambda = 550$ nm ($\varepsilon = 38,650$ cm$^{-1}$M$^{-1}$). Concentrations of $4$-methylanilinium, $4$-methylaniline, and methyl orange at each titration point were calculated based on the concentration protonated methyl orange (determined by UV-vis) and the initial concentrations of all reagents. Linear regression of a plot of (($4$-CH$_3$-aniline)/[$4$-CH$_3$-anilinium][MOH$^+$]) was used to determine the $pK_a$ of $4$-methylanilinium: $pK_a = pK_a$(methyl orange) − log(slope).
Figure S2. Spectrophotometric titration of 11 µM methyl orange with 4-methylanilinium. Above 350 nm, the 4-methylanilinium extinction coefficient does not exceed 0.4 cm⁻¹M⁻¹, four orders of magnitude less than methyl orange and protonated methyl orange and therefore does not contribute significantly to the overall absorbance signal.

Figure S3. The slope of (([4-CH₃-aniline]/[4-CH₃-anilinium])[MOH]) versus [MO] \((m = 0.15)\) can be used to determine the \(pK_a\) for 4-methylanilinium \((pK_a = 11.4)\). \(R^2 = 0.997\).
4-iodoanilinium tetrafluoroborate

**Figure S4.** $^1$H NMR of 4-iodoanilinium tetrafluoroborate in CD$_3$CN.

To determine the p$K_a$ of 4-iodoanilinium, a spectrophotometric titration was performed following the same procedure as described for 4-methylanilinium, except that 3-nitroaniline was used as the indicator (p$K_a = 7.68$), and there was a minor contribution from the 4-iodoanilinium absorbance that had to be subtracted out.

**Figure S5.** Spectrophotometric titration of 0.865 mM 3-nitroaniline with 4-iodoanilinium. The absorbance for 4-iodoanilinium is shown in red. This contribution to the overall absorbance signal was subtracted out (proportional to its concentration) in the making of Figure S6 to determine the p$K_a$ of 4-iodoanilinium.
Figure S6. The slope of \( \frac{([4-I\text{-}aniline]/[4-I\text{-}anilinium])^{*}[3-\text{NO}_2\text{-}anilinium]}{[3-\text{NO}_2\text{-}aniline]} \) versus \([3-\text{NO}_2\text{-}aniline]\) \(m = 0.025966\) can be used to determine the \(pK_a\) for 4-iodoanilinium \(pK_a = 9.27\). \(R^2 = 0.986\).
Table S1. $pK_a$ values of para-substituted anilinium derivatives in acetonitrile, rate constants for reaction with Ni$^{II}$H

<table>
<thead>
<tr>
<th>Acid</th>
<th>para-substituent</th>
<th>$pK_a$</th>
<th>Reference</th>
<th>$k$ (M$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>4-methoxyanilinium</td>
<td>–OCH$_3$</td>
<td>11.86</td>
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<td>7</td>
</tr>
<tr>
<td>4-methylanilinium</td>
<td>–CH$_3$</td>
<td>11.4</td>
<td>this work</td>
<td>15.8</td>
</tr>
<tr>
<td>4-tertbutylanilinium</td>
<td>–C(CH$_3$)$_3$</td>
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<td>1</td>
<td>16.2</td>
</tr>
<tr>
<td>anilinium</td>
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<td>10.62</td>
<td>2</td>
<td>58 (Ref. 3)</td>
</tr>
<tr>
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<td>9.7</td>
<td>1</td>
<td>194</td>
</tr>
<tr>
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<td>–Br</td>
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<tr>
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<td>–OCF$_3$</td>
<td>9.28</td>
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<td>199</td>
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<tr>
<td>4-iodoanilinium</td>
<td>–I</td>
<td>9/27</td>
<td>this work</td>
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<td>4-cyanoanilinium</td>
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<td>762</td>
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</tbody>
</table>

Stopped flow kinetics traces and observed rate constant versus concentration data for each acid

4-methoxyanilinium

![Stopped flow kinetics traces](image)

Figure S7. Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various concentrations of 4-(methoxy)anilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 7 M$^{-1}$s$^{-1}$, $R^2 = 0.997$) represents the fit of the data with the intercept fixed at the origin.
**4-methylanilinium**

![Graphs](image1)

**Figure S8.** Left: Stopped-flow kinetics traces for the reaction of Ni^{II}H with various concentrations of 4-methylanilinium to generate H₂ and Ni^{II} (λ_{obs} = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 15.8 M⁻¹s⁻¹, R² = 0.999) represents the fit of the data with the intercept fixed at the origin.

**4-tertbutylanilinium**

![Graphs](image2)

**Figure S9.** Left: Stopped-flow kinetics traces for the reaction of Ni^{II}H with various concentrations of 4-tertbutylanilinium to generate H₂ and Ni^{II} (λ_{obs} = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 16.2 M⁻¹s⁻¹, R² = 0.999) represents the fit of the data with the intercept fixed at the origin.
4-chloroanilinium

Figure S10. Left: Stopped-flow kinetics traces for the reaction of NiH with various concentrations of 4-chloroanilinium to generate H₂ and NiII (λₜₐₜ = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 194 M⁻¹s⁻¹, R² = 0.998) represents the fit of the data with the intercept fixed at the origin.

4-bromoanilinium

Figure S11. Left: Stopped-flow kinetics traces for the reaction of NiH with various concentrations of 4-bromoanilinium to generate H₂ and NiII (λₜₐₜ = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 220 M⁻¹s⁻¹, R² = 0.997) represents the fit of the data with the intercept fixed at the origin.
4-trifluoromethoxyanilinium

**Figure S12.** Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various concentrations of 4-trifluoromethoxyanilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 199 M$^{-1}$s$^{-1}$, $R^2 = 0.995$) represents the fit of the data with the intercept fixed at the origin.

4-iodoanilinium

**Figure S13.** Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various concentrations of 4-iodoanilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 220 M$^{-1}$s$^{-1}$, $R^2 = 0.997$) represents the fit of the data with the intercept fixed at the origin.
4-(methylbenzoate)anilinium

Figure S14. Left: Stopped-flow kinetics traces for the reaction of NiIIH with various concentrations of 4-(methylbenzoate)anilinium to generate H2 and NiII (λobs = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 553 M⁻¹s⁻¹, R² = 0.996) represents the fit of the data with the intercept fixed at the origin.

4-trifluoromethylanilinium

Figure S15. Left: Stopped-flow kinetics traces for the reaction of NiIIH with various concentrations of 4-trifluoromethylanilinium to generate H2 and NiII (λobs = 500 nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 538 M⁻¹s⁻¹, R² = 0.997) represents the fit of the data with the intercept fixed at the origin.
4-cyanoanilinium

Figure S16. Left: Stopped-flow kinetics traces for the reaction of NiIIH with various concentrations of 4-cyanoanilinium to generate H2 and NiII ($\lambda_{\text{obs}} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted vs. acid concentration. Blue line (slope = 762 M$^{-1}$ s$^{-1}$, $R^2 = 0.997$) represents the fit of the data with the intercept fixed at the origin.

Hammett Plot

As discussed in the main text, the data in Figure 1 can also be displayed in a Hammett format. We accomplish this using the $\sigma_p$ values of the para-substituents from the literature$^5$ for the horizontal axis and log($K/K_H$) for the vertical axis. Because $\sigma_p$ and p$K_a$ are related values, Figure 1 and Figure S17 are very similar in appearance and the same information can be inferred from each.

Figure S17. Hammett plot derived from the rate constants reported in Table S1.
SI–3 Base:Acid Ratios

Stopped flow kinetics traces and observed rate versus [base] data for each acid

tetrabutylammonium trifluoroacetate: trifluoroacetic acid

Figure S18. Left: Stopped-flow kinetics traces for the reaction of Ni^III_H with various ratios of trifluoroacetate:trifluoroacetic acid to generate H2 and Ni^II (λ_{obs} = 500 nm). The shift in absorbance for the slower datasets (higher base concentration), appeared to arise from the formation of some precipitate upon mixing. This was only seen with TFA. Right: Observed rate constant obtained from kinetics traces plotted against base concentration. Trifluoroacetic acid concentration was fixed at 9.5 mM, trifluoroacetate varied.

4-methylaniline:4-methylanilinium tetrafluoroborate

Figure S19. Left: Stopped-flow kinetics traces for the reaction of Ni^III_H with various ratios of 4-methylaniline:4-methylanilinium to generate H2 and Ni^II (λ_{obs} = 500 nm). The decrease in final absorbance as base concentration is increased is a result of equilibrium formation as Ni^III can split H2 in the presence of a strong base. Right: Observed rate constant obtained from kinetics traces plotted against base concentration. 4-methylanilinium concentration was fixed at 6.77 mM, base was varied.
**Figure S20.** Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various ratios of aniline:anilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500$ nm). The decrease in final absorbance as base concentration is increased is a result of equilibrium formation as Ni$^{II}$ can split H$_2$ in the presence of a strong base. Right: Observed rate constant obtained from kinetics traces plotted against base concentration. Anilinium concentration was fixed at 5 mM, base was varied.

**Figure S21.** Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various ratios of 4-bromoaniline:4-bromoanilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted against base concentration. 4-bromoanilinium concentration was fixed at 5 mM, base was varied.
**4-(methylbenzoate)aniline:4-(methylbenzoate)anilinium tetrafluoroborate**

Figure S22. Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}H$ with various ratios of 4-(methylbenzoate)aniline:4-(methylbenzoate)anilinium to generate H$_2$ and Ni$^{III}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted against base concentration. 4-(methylbenzoate)anilinium concentration was fixed at 1.6 mM, base was varied.

**4-trifluoromethylaniline:4-trifluoromethylanilinium tetrafluoroborate**

Figure S23. Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}H$ with various ratios of 4-trifluoromethylaniline:4-trifluoromethylanilinium to generate H$_2$ and Ni$^{III}$ ($\lambda_{obs} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted against base concentration. 4-trifluoromethylanilinium concentration was fixed at 3.1 mM, base was varied.
Figure S24. Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various ratios of 4-cyanoaniline:4-cyanoanilinium to generate H$_2$ and Ni$^{II}$ ($\lambda_{\text{obs}} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted against base concentration. 4-cyanoanilinium concentration was fixed at 1 mM, base was varied.

dimethylformamide:dimethylformamidium triflate

Figure S25. Left: Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with various ratios of dimethylformamide:dimethylformamidium to generate H$_2$ and Ni$^{II}$ ($\lambda_{\text{obs}} = 500$ nm). Right: Observed rate constant obtained from kinetics traces plotted against base concentration. dimethylformamidium concentration was fixed at 1 mM, base was varied.
Figure S26. Normalized rate constant plotted vs. base:acid ratio. Observed first order rate constants determined in the presence of base were normalized to the observed first order rate constant in the absence of base. In each case, the acid concentration was held constant and the base concentration was varied. Trifluoroacetic acid (TFA, $pK_a = 12.65$, 9.5 mM), 4-methylanilinium (4-Me, $pK_a = 11.4$, 3.4 mM), anilinium (4-H, $pK_a = 10.62$, 5 mM), and 4-bromoanilinium (4-Br, $pK_a = 9.43$, 5 mM), dimethylformamidium (DMF, $pK_a = 6.1$, 1 mM), 4-trifluoromethylanilinium (4-CF$_3$, $pK_a = 8.03$, 3.1 mM), 4-(methylbenzoate)anilinium (4-COOMe, $pK_a = 8.6$, 1.6 mM), and 4-cyanoanilinium (4-CN, $pK_a = 7$, 1 mM), are represented here. The acids with a $pK_a$ values lower than 9 did not follow any trend, in keeping the $pK_a$ independence shown for this range in Figure 1. Markers represent actual data points; lines in between are a guide for the eye.
**SI–4 Homoconjugation**

**Determination of the homoconjugation constant for 4-cyanoanilinium**

$^1$H NMR was used to determine the homoconjugation constant for 4-cyanoanilinium. In the case that a proton is rapidly exchanging between multiple locations, only one peak will appear. The shift of that peak is dependent upon the shift of each pure species and the percentage of protons in each state. For 4-cyanoanilinium, this is represented as equation S1, where $\delta$ is the observed shift, $\%H_X$ is the percentage of protons in state X, $\delta_X$ is the shift for pure X. For 4-cyanoanilinium, there are three possible states, B (4-cyanoaniline), BH (4-cyanonanilinium), and BHB (homoconjugated species).

$$\delta = \%H_B \delta_B + \%H_{BH} \delta_{BH} + \%H_{BHB} \delta_{BHB}$$  \hspace{1cm} (S1)

Because each of the species present contains a different number of protons participating in the exchange process, we have to account for this using equation S2, where $n$ represents the number of exchanging protons on species X and $\chi_X$ represents the mole fraction of species X.

$$\%H_X = \frac{n\chi_X}{2\chi_B + 3\chi_{BH} + 5\chi_{BHB}}$$  \hspace{1cm} (S2)

$$\delta = \frac{2\chi_B \delta_B + 3\chi_{BH} \delta_{BH} + 5\chi_{BHB} \delta_{BHB}}{2\chi_B + 3\chi_{BH} + 5\chi_{BHB}}$$  \hspace{1cm} (S3)

To relate equation S3 to the homoconjugation constant, we must solve for the concentration of the homoconjugated species in the equilibrium equation. As is explained below in the experiment description, we simplified our analysis by using a 1:1 ratio of B and BH and then varied the total concentration. Thus, we simplify the input concentration of B and BH to be represented as $[I]_0$

$$[I]_0 = [B]_0 = [BH]_0$$  \hspace{1cm} (S4)

$$K = \frac{[BHB]}{[B][BH]} = \frac{[BHB]}{([I]_0 - [BHB])^2}$$  \hspace{1cm} (S5)

$$[BHB] = [I]_0 + \frac{1 - \sqrt{1 + 4K[I]_0}}{2K}$$  \hspace{1cm} (S6)

$$\chi_B = \chi_{BH} = \frac{([I]_0 - [BHB])}{2([I]_0 - [BHB]) + [BHB]} = \frac{([I]_0 - [BHB])}{2[I]_0 - [BHB]}$$  \hspace{1cm} (S7)

$$\chi_{BHB} = \frac{[BHB]}{2([I]_0 - [BHB]) + [BHB]} = \frac{[BHB]}{2[I]_0 - [BHB]}$$  \hspace{1cm} (S8)
Substituting S7 and S8 into S3 results in:

\[
\delta = \frac{2([I]_0 - [BHB])\delta_B + 3([I]_0 - [BHB])\delta_{BH} + 5[BHB]\delta_{BHB}}{5[I]_0} \tag{S9}
\]

Equation S9 can be further simplified by acknowledging that \(\delta_B\) and \(\delta_{BH}\) can be represented as a single parameter, \(\delta_I\).

\[
\delta_I = \frac{2}{5} \delta_B + \frac{3}{5} \delta_{BH} \tag{S10}
\]

\[
\delta = \frac{([I]_0 - [BHB])}{[I]_0} \delta_I + \frac{[BHB]}{[I]_0} \delta_{BHB} \tag{S11}
\]

Substituting in S6 into S11 we obtain our fitting equation for our NMR shift, with three dependent variables \(K\), \(\delta_I\), and \(\delta_{BHB}\).

\[
\delta = \frac{\sqrt{1 + 4K[I]_0} - 1}{2K[I]_0} \delta_I + \left(1 + \frac{1 - \sqrt{1 + 4K[I]_0}}{2K[I]_0}\right) \delta_{BHB} \tag{S12}
\]

The homoconjugation constant was therefore determined by the average of three separate experiments. Each experiment followed a generic procedure in which 1 mL of a deuterated acetonitrile stock solution of 1:1 4-cyanoaniline:4-cyanoanilinium was prepared in an inert atmosphere glovebox. To three separate J-Young tubes, 0.125 mL, 0.25 mL, and 0.5 mL of stock solution were added. Each was then diluted to 0.5 mL total. After taking NMRs, the solutions were each then diluted by 0.1 mL. This was repeated 5-6 times to complete a dataset. After referencing the proteo-impurity of acetonitrile to 1.94 ppm, the peak location of the acidic protons was recorded. After plotting the chemical shift against the input concentration, \([I]_0\), the datasets were fit using equation S12 (Figure S27).
**Figure S27.** Three titrations of 1:1 mixtures of 4-cyanoaniline:4-cyanoanilinium in deuterated acetonitrile. The fits represent equations S12. The average value for $K$ from the three datasets was $1.24 \pm 0.38 \text{ M}^{-1}$.

**Tosic Acid Kinetic Trace**

**Figure S28.** Stopped-flow kinetics trace for the reaction of Ni$^{III}$H with 5 mM of tosic acid to generate H$_2$ and Ni$^{II}$ ($\lambda_{obs} = 500 \text{ nm}$). Fit, shown in red, gives an observed rate constant of 640 s$^{-1}$. 
**SI–5 Acid Concentration Independence**

**Figure S29.** Observed rate constant plotted against dimethylformamidium concentration; rate data obtained from stopped-flow kinetics traces monitoring the appearance Ni\textsuperscript{II} (\(\lambda_{\text{obs}} = 500\) nm). The colored data points represent separate experiments. While the observed rate constant always plateaued around 10 mM DMFH\textsuperscript{+}, the rate constant at which it plateaued at was inconsistent.

**Figure S30.** Observed rate constant plotted against p-cyanoanilinium concentration; rate data obtained from stopped-flow kinetics traces monitoring the appearance of Ni\textsuperscript{II} (\(\lambda_{\text{obs}} = 500\) nm).
**SI–6 Water in acetonitrile**

**Water addition to anilinium**

Figure 5 in the main text shows that adding water to strong acids (p$K_a < 8$) results in an increase in the catalytic rate. As discussed, this is attributed to hydronium (or hydronium hydrate) formation in solution. In support of this statement, we find that the addition of water to anilinium (p$K_a = 10.6$) does not result in an increase in rate constant (Figure S31).

![Figure S31](image)

**Figure S31.** Stopped-flow kinetics traces for the reaction of Ni$^{II}$H with 10 mM anilinium in the presence of H$_2$O to generate H$_2$ and Ni$^{III}$. 
**SI-7 Trifluoroacetic acid dimerization**

**Second Order Reactivity and Dimerization**

It was reported in the literature that no dimerization is observed with trifluoroacetic acid in acetonitrile. Obtaining second order kinetics for the acids only has two possible explanations, either a termolecular reaction is occurring (i.e. Rate = k[NiH][AH]2) or the acid is dimerizing (i.e. Rate = k[NiH][(AH)2]) with a small enough dimerization constant such that [(AH)₂] ∝ [AH]². We obtained an upper bound for the dimerization constant of 1 M⁻¹ to see second order reactivity by determining that point at which [(AH)₂] ∝ [AH]² no longer held true (Figure S32).

![Figure S32](image.png)

**Figure S32.** Expected concentration of (AH)₂, normalized to one at the highest input concentration of AH, [AH]₀, (chosen to match the concentrations in the trifluoroacetic acid experiment), given a dimerization constant of 10, 1, and 0.1 M⁻¹. The black line represents a true second order curve. At 1 M⁻¹ we see a slight deviation from second order and anything higher than that would no longer give a satisfactory fit to second order kinetics, suggesting that if trifluoroacetic acid and trichloroacetic acid are dimerizing, the dimerization constant is below 1 M⁻¹.

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References


(4) Rountree, E. S.; Martin, D. J.; McCarthy, B. D.; Dempsey, J. L. *ACS Catalysis* **2016**. DOI: 10.1021/acscatal.6b00667.
