Benchmarking Density Functionals, Basis Sets, and Solvent Models in Predicting Thermodynamic Hydricities of Organic Hydrides

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1 Abstract

Many renewable energy technologies, such as hydrogen gas synthesis and carbon dioxide reduction, rely on chemical reactions involving hydride anions ($\text{H}^-$). When selecting molecules to be used in such applications, an important quantity to consider is the thermodynamic hydricity, which is the free energy required for a species to donate a hydride anion. Theoretical calculations of thermodynamic hydricity depend on several parameters, mainly the density functional, basis set, and solvent model. In order to assess the effects of the above three parameters, we carry out hydricity calculations for a set of molecules with known experimental hydricity values, generate linear fits, and compare the $R$-squared, root-mean-squared error (RMSE), and Akaike Information Criterion (AIC) across different combinations of density functionals, basis sets, and solvent models. Based on these results we are able to quantify the accuracy of theoretical predictions of hydricity and recommend the parameters with the best compromise between accuracy and computational cost.

2 Introduction

The hydricity of a molecule is given by

$$\Delta G_{\text{H}^-} = G(\text{acceptor}) + G(H^-) - G(\text{donor}),$$

meaning it measures the free energy difference before and after a hydride transfer reaction. Hydride transfer reactions play a crucial role in various renewable energy
technologies, such as the electrochemical reduction of CO$_2$ into carbon-based fuels [1, 2, 3, 4, 5, 6] or H$_2$ synthesis [4, 7].

Traditionally, transition metal hydrides have been the most popular candidates for such applications [8], but many of these metals are expensive, unsustainable, and toxic [9]. Organic hydrides such as dihydropyridine [1, 2] and benzimidazoles [3] are promising metal-free, renewable alternatives to their costly counterparts. Therefore, studying the hydricities of organic compounds in the hopes of selecting more metal-free catalysts for CO$_2$ reduction would be a valuable effort towards closing the carbon cycle.

However, the hydricity is expensive and laborious to measure experimentally; it involves summing equilibrium constants, acid dissociation constants, and free energies over several thermochemical reactions [5], not to mention having to synthesize the molecule of interest in the first place. There have been several works that use Kohn-Sham density functional theory (DFT) to theoretically predict hydricities. Ref. [9] calculated the hydricities of several metal-free hydrides via two different approaches specified in [10] and [11]. Ref. [12] calculated the hydricities of various p- and o-quinones in DMSO with geometry optimizations done using B3LYP/6-31+G*, single point calculations using B3LYP/6-311++G and MP2/6-311++G**, and correction terms calculated using B3LYP/6-31+G*, with solvent model IEFPCM for all steps of the calculation. Ref. [13] calculated the hydricities of 6d transition metal hydrides using B3LYP as the density functional, LACVP** and LACV3P++** as the basis set for the geometry optimization/frequency analysis and single point calculations, respectively, and the Poisson-Boltzmann solvent model.

These works all use 2 selected methods for the entire set of tested molecules, rather than testing several different methods and observing the effects. A benchmark of DFT methods for calculating hydricities did not exist until July 2021 [14], and this benchmark was exclusively for 3d transition metal complexes, while we provide a benchmark for organic hydrides.

When using density functional theory to calculate hydricity, the three most important parameters to consider are the density functional, basis set, and solvent model. In this paper, we test different combinations of these three parameters, all stemming from the "base" level of theory, which uses B3LYP as the functional, TZVP as the basis set, and PCM as the solvent model. We will first summarize the systems we studied and the methods we used to calculate their hydricities. Then we will introduce the statistical measures we utilized to compare performance across different models. From these results we were able to formulate a set of guidelines for carrying out theoretical calculations of thermodynamic hydricities for organic hydrides. We end by discussing concluding thoughts and future directions.

3 Methods

Figure 1 lists the donor structures for all the molecules we tested, along with their experimentally measured hydricity. Starting structures were obtained from WebCSD,
an online crystal structure database provided by the Cambridge Crystallographic Data Centre and Leibniz Institute for Information Infrastructure. Any structures not available on WebCSD were built by hand on GaussView, a graphical interface used for preparing input files for quantum chemistry calculations. In such cases, we took special care to make the initial structures as close to the expected final structures as possible by manually adjusting bond angles.

For molecules numbered 20-27, we ran geometry optimizations on different acceptor structures to determine the hydridic hydrogen, i.e. the H that is donated in a hydride transfer reaction. For molecules 1 and 10, the donor structures have charge -1 and acceptor structures charge 0. For the others the donor structures have charge 0 and acceptor structures charge +1. All molecules are solvated in either acetonitrile or dimethylsulfoxide (DMSO).

Table 1 gives the combinations of density functionals, basis sets, and solvent models used for our calculations. BP86, which has the lowest computational cost of the density functionals we used, is a generalized gradient approximation (GGA) functional, meaning it only uses the local electron density and gradient. B3LYP is the most widely used hybrid functional, i.e. it mixes the DFT exchange-correlation energy and Hartree-Fock (HF) exchange energy with a fixed ratio [21, 22, 23]. B3LYP has 20% HF exchange, while B3LYP* has 15% [24]. ωB97X-D3, the most computationally expensive out of the three functionals used, is a range separated hybrid functional, meaning the mixing ratio of the DFT and HF contributions vary depending on the distance between electrons [21, 25]. B3LYP has 3 empirical parameters fitted to experiment, while ωB97X-D3 has 17 [22, 23, 26].

For the basis sets, we selected 6-31G*, TZVP, and TZVP+ (short for ma-def2-TZVP(-f)-LTZ+), which have 14, 19, and 28 basis functions per carbon atom, respectively [27, 28, 29, 30]. For any atoms beyond potassium (K), 6-31G* is replaced by the LANL2DZ (LDZ) basis set and an effective core potential (ECP), while and TZVP and TZVP+ are replaced by the LANL2TZ (LTZ) basis set and an ECP [31, 32, 33]. TZVP+ is not only larger than TZVP, but also has the f functions removed and diffuse functions added to non-hydrogen atoms [27].

Lastly, we used two continuum solvent models for our calculations: C-PCM ISWIG (PCM for short) and SMD. C-PCM ISWIG is a conductor-like polarizable continuum solvent model (C-PCM) with a "smooth discretization" via the Improved Switching/Gaussian (ISWIG) method. Polarizable continuum models represent the solvent by placing the solute in a cavity with an apparent charge distribution over the surface of that cavity. Boundary-element methods are used to discretize the solute/continuum interface, but this often leads to a discontinuous potential energy surface for the solute, leading to singularities. The ISWIG method is a discretization scheme that overcomes such limitations [34, 35]. SMD is another type of polarizable continuum solvent model, but it accounts for short-range solvent-solute interactions such as dispersion and solvent structural effects (e.g. hydrogen bonding or exchange repulsion), whereas regular polarizable continuum models only account for bulk electrostatic interactions [36].
| Model ID | Level of Theory 1                        | Level of Theory 2                        |
|----------|----------------------------------------|----------------------------------------|
| D01      | B3LYP/6-31G*/PCM                       |                                        |
| D02      | B3LYP/TZVP/PCM                         |                                        |
| D03      | ωB97X-D3/TZVP/PCM                      |                                        |
| D04      | BP86/TZVP/PCM                          |                                        |
| D05      | B3LYP/TZVP/Gas                         |                                        |
| D06      | B3LYP/6-31G*/Gas                       |                                        |
| D07      | B3LYP*/TZVP/PCM                        |                                        |
| D08      | B3LYP/6-31G*/PCM                       | B3LYP/TZVP/PCM                         |
| D09      | B3LYP/TZVP/PCM                         | B3LYP/TZVP+/PCM                        |
| D10      | B3LYP/6-31G*/Gas                       | B3LYP/6-31G*/PCM                       |
| D11      | B3LYP/TZVP/Gas                         | B3LYP/TZVP/PCM                         |
| D12      | ωB97X-D3/TZVP/PCM                      | ωB97X-D3/TZVP+/PCM                     |
| D13      | ωB97X-D3/6-31G*/PCM                    |                                        |
| D14      | B3LYP/TZVP/Gas                         | B3LYP/TZVP/SMD                         |
| D15      | B3LYP/TZVP/PCM                         | B3LYP/TZVP/SMD                         |

Table 1: Combinations of parameters used. Each level of theory is specified in the following format: density functional/basis set/solvent model.

For models that have two columns, the first column indicates the level of theory used for the geometry optimization and frequency analysis calculations, while the second column indicates the level of theory used for the single point calculations. This composite approach allows for using more expensive levels of theory while keeping computational cost low, as geometry optimization and frequency analysis calculations involve taking many gradients while single point calculations do not. If a model has a single column, the same level of theory was used for all calculations. Levels of theory using SMD as the solvent model were calculated using Q-Chem [37], while others were calculated using TeraChem [38].

The free energies of the acceptor and donor can easily be calculated on TeraChem and Q-Chem, but the free energy of the solvated hydride is difficult to compute using such methods. A hydride anion has complicated interactions with the solvent that a continuum solvent model cannot account for. Even if we were to use an explicit solvent model in an attempt to calculate the free energy of the hydride, the hydride will quickly react with surrounding molecules, making it extremely difficult to obtain a reasonable estimate of its free energy in solvent. There are several ways to circumvent this problem. Ref. [10] calculated the free energy of the hydricity half reaction

\[
\Delta G_{\text{HHR}} = G(\text{acceptor}) - G(\text{donor})
\]  

then used a reference reaction to evaluate \(G(H^-)\) and construct the thermodynamic hydricity via an isodesmic reaction scheme

\[
\text{AH}^- + \text{B} \rightarrow \text{A} + \text{BH}^-, \tag{3}
\]
where \( AH^- \) and \( BH^- \) are the donor structures of species A and B, respectively. Meanwhile, Ref. [14] used a thermochemical cycle given by

\[
MH + H^+ \rightleftharpoons M^+ + H_2 \tag{4}
\]

\[
H_2 \rightleftharpoons H^+ + H^- \tag{5}
\]

and modeled the protons as a complex with discrete solvent molecules.

In this paper, we chose to calculate the free energy of the hydricity half reaction and treat the free energy of the solvated hydride as a fitting parameter. More specifically, we compute the \( \Delta G_{HHR} \) for all molecules using one model, create a linear fit with the slope fixed at 1, and apply an overall vertical shift to all the data points so that the linear fit goes through the origin. This vertical shift corresponds to the free energy of the hydride, and the final linear fit for all our data sets are \( y=x \). Then we calculate the R-squared, root-mean-squared error, and Akaike information criterion (AIC) for each data set to quantify the accuracy of the given model.

For this benchmark, we used the AIC as a tool to verify that each model’s performance is statistically significant. For instance, when model A gives a better R-squared and RMSE compared to model B, we want to confirm that this result is due to model A truly being more accurate than model B, and not because of random statistical fluctuations. That is, if we sample some noise from a Gaussian distribution and apply it to the data set produced by model B, the new linear fit better not give a better R-squared and RMSE value compared to that of model A. This is in theory what a P-value measures, but it is flawed in that the choice of cutoff for determining statistical significance is rather arbitrary. Bootstrapping could be another alternative, but we would have to perform many iterations to get the desired degree of confidence. This is why we chose the AIC, whose difference across different models serves the same purpose as P-values [39], as our measure of statistical significance.

For our data, we used the second order AIC for small sample sizes

\[
AIC = -2 \ln L + 2K + \frac{2K(K+1)}{n-K-1} \tag{6}
\]

which is applicable for \( \frac{n}{K} < 40 \), where \( n \) is the sample size and \( K \) is the number of model parameters. Since our model is a linear fit with data points that do not lie exactly on the line, \( K = 3 \). \( -2 \ln L \) is given by

\[
-2 \ln L = \sum_i \left( \frac{(a_i - x_i)^2}{\sigma^2} + 2 \ln \sqrt{2\pi\sigma} \right) \tag{7}
\]

where \( a_i \) are the values that the model predicts, \( x_i \) are the actual values, and \( \sigma \) is the uncertainty. Since the uncertainty is unknown for our models, we perform an iteration process to find the uncertainty that maximizes the likelihood function \( L \) for each model.
To compare the AIC across the different models, we calculate the exponential of the AIC differences, or the relative likelihood:

\[ e^{\frac{1}{2}(AIC_{\text{min}} - AIC_i)} \]  

which is proportional to the \(i\)th model’s probability for minimizing information loss. We have disregarded the normalization factor that would give us the AIC weights for convenience. The model with the lowest AIC (AIC\(_{\text{min}}\)) has a relative likelihood of exactly 1. Since the \(n\) and \(K\) of all our models are the same, the \(2K + \frac{2K(K+1)}{2}\) terms cancel when computing the relative likelihood, leaving only the log-likelihood terms in the exponent. [40]

4 Results and Discussion

| Model ID | \(R^2\)  | RMSE  | AIC    | \(e^{\frac{1}{2}(AIC_{\text{min}} - AIC_i)}\) |
|----------|----------|-------|--------|-----------------------------------------------|
| D01      | 0.967    | 5.308 | 229.501| 1.428E-02                                     |
| D02      | 0.967    | 5.171 | 231.262| 5.921E-03                                     |
| D03      | 0.983    | 4.040 | 225.891| 8.684E-02                                     |
| D04      | 0.962    | 5.448 | 235.144| 8.500E-04                                     |
| D05      | 0.648    | 31.488| 291.506| 4.904E-16                                     |
| D06      | 0.629    | 33.267| 293.782| 1.571E-16                                     |
| D07      | 0.966    | 5.268 | 231.931| 4.238E-03                                     |
| D08      | 0.969    | 5.053 | 231.478| 5.315E-03                                     |
| D09      | 0.962    | 5.594 | 232.433| 3.296E-03                                     |
| D10      | 0.967    | 5.322 | 227.716| 3.486E-02                                     |
| D11      | 0.967    | 5.178 | 231.121| 6.353E-03                                     |
| D12      | 0.981    | 4.246 | 225.294| 1.170E-01                                     |
| D13      | 0.979    | 4.496 | 221.003| 1                                             |
| D14      | 0.969    | 5.056 | 228.760| 2.068E-02                                     |
| D15      | 0.969    | 5.042 | 228.111| 2.861E-02                                     |

Table 2: R-squared, RMSE, AIC, and relative likelihood for molecules in acetonitrile.
Figure 1: Figure of all molecules tested. Hyridic hydrogens are colored red. The listed numbers are experimentally determined hydricities, with the superscripts indicating reference. Numbers with no parenthesis were obtained in acetonitrile, while those with parenthesis were obtained in DMSO. a: Ref. [15], b: Ref. [16], c: Ref. [17], d: Ref. [6], e: Ref. [11], f: Ref. [18], g: Ref. [19], h: Ref. [20], i: Ref. [9].
Figure 2: Two example calculated vs experimental hydricity plots for molecules in acetonitrile. Each data point is labeled by the corresponding molecule number given in Figure 1. The calculated values were obtained using a) D03 (ωB97X-D3/TZVP/PCM), one of our most accurate models b) D06 (B3LYP/6-31G*/Gas), one of our least accurate models.
Table 3: R-squared, RMSE, AIC, and relative likelihood for molecules in DMSO.

| Model ID | $R^2$ | RMSE | AIC  | $\text{e}^{\frac{1}{2}(\text{AIC}_{\text{min}}-\text{AIC}_i)}$ |
|----------|-------|------|------|------------------------------------------------|
| D01      | 0.779 | 9.213| 229.006| 1.714E-02                                      |
| D02      | 0.760 | 9.850| 230.820| 6.919E-03                                      |
| D03      | 0.771 | 10.456| 225.773| 8.633E-02                                      |
| D04      | 0.745 | 9.469| 234.472| 1.115E-03                                      |
| D05      | 0.715 | 12.234| 291.466| 4.688E-16                                      |
| D06      | 0.745 | 11.136| 293.742| 1.502E-16                                      |
| D07      | 0.760 | 9.709| 231.434| 5.090E-03                                      |
| D08      | 0.763 | 9.852| 231.012| 6.287E-03                                      |
| D09      | 0.764 | 9.600| 231.928| 3.977E-03                                      |
| D10      | 0.787 | 9.054| 227.269| 4.085E-02                                      |
| D11      | 0.760 | 9.954| 230.713| 7.301E-03                                      |
| D12      | 0.778 | 10.075| 225.118| 1.197E-01                                      |
| D13      | 0.805 | 9.317| 220.873| 1                                             |
| D14      | 0.778 | 9.668| 228.384| 2.340E-02                                      |
| D15      | 0.784 | 9.461| 227.712| 3.274E-02                                      |

Figure 3: Comparison of R-squared and RMSE values across different density functionals, with TZVP as the basis set and PCM as the solvent model.

From Figure 3, we can see that $\omega$B97X-D3 gives the best accuracy, as expected. The result for $\omega$B97X-D3/TZVP/PCM in DMSO seems to be inconclusive at first sight, since it gives an R-squared value closest to 1 while giving the largest RMSE. However, the relative likelihood plots (Figures 8 and 9) confirm that $\omega$B97X-D3 is indeed the most accurate density functional. It is also apparent that the effect of using B3LYP* instead B3LYP is minimal; this is because B3LYP* was originally developed to more accurately predict low-spin/high spin energy splitting in molecules with multiple spin configurations, i.e. transition metal complexes [21]. Since we are only working with or-
ganic hydrides, changing the percentage of HF exchange will not impact the calculated hydricity in a meaningful manner.

![Graph showing R-squared and RMSE values across different basis sets, with B3LYP as the density functional and PCM as the solvent model.](image1)

Figure 4: Comparison of R-squared and RMSE values across different basis sets, with B3LYP as the density functional and PCM as the solvent model.

![Graph showing R-squared and RMSE values across different basis sets, with ωB97X-D3 as the density functional and PCM as the solvent model.](image2)

Figure 5: Comparison of R-squared and RMSE values across different basis sets, with ωB97X-D3 as the density functional and PCM as the solvent model.

Looking at Figures 4 and 5, it is clear that using a bigger basis set does not necessarily give better results. When using B3LYP as the density functional, TZVP performed worse than 6-31G*, and using TZVP for the geometry optimization/frequency analysis and TZVP+ for the single point calculation also gave a slightly worse accuracy than using 6-31G* and TZVP. With ωB97X-D3 as the density functional, TZVP performed best for acetonitrile while 6-31G*, the smallest basis set, gave the best accuracy. This is not surprising given that our test molecules were all organic hydrides, meaning we rarely have atoms beyond K. For users looking to calculate the hydricity of an organic...
molecule, we would recommend using a basis set no larger than TZVP, considering the trade-off between computational cost and accuracy.

Figure 6: Comparison of R-squared and RMSE values across different solvent models, with B3LYP as the density functional and 6-31G* as the basis set.

Figure 7: Comparison of R-squared and RMSE values across different solvent models, with B3LYP as the density functional and TZVP as the basis set.

From Figures 6 and 7, we can conclude that the solvent model can be turned off for geometry optimization and frequency analysis calculations. We can also see that turning off the solvent model for the single point calculation has a minimal impact on accuracy for molecules in DMSO compared to those in acetonitrile. This is because the effect of using a continuum solvent model is largely influenced by the net charge of the solute, and we apply the same vertical shift to all data points in a single data set. If all molecules in a data set have the same charge, such as those in DMSO, the near-identical effect of turning off the solvent model is effectively “cancelled out” by the vertical shift. However, if any molecules have a different charge compared to the
rest of the data set, like molecules 1 and 10 in acetonitrile, their calculated hydricities differ drastically from the other molecules, leading to the result shown in Figure 2b.

Comparing the effects of using PCM versus SMD, SMD does perform slightly better than PCM but the difference is minimal. SMD calculations take considerably longer than PCM calculations to both set up and run, and they are also more prone to convergence failures. This leads us to recommend using PCM when calculating the hydricity of an organic hydride.

Figure 8: Log-scale plot of relative likelihood values for molecules in acetonitrile.

Figure 9: Log-scale plot of relative likelihood values for molecules in DMSO.

Lastly, we examine the relative likelihoods of each method to test the statistical significance of our results. Most methods give a log-scale relative likelihood on the order of $10^{-2}$. Looking at models that used $\omega$B97X-D3 (D03, D12, D13), we can see that all such models gave a relative likelihood noticeably closer to 1 (closer to 0 in log-scale) compared to other methods, giving us confidence that the improved accuracy coming from using $\omega$B97X-D3 over other density functionals is statistically significant. The relative likelihoods of methods using no solvent model at all (D05, D06) show that the improvements coming from using a solvent model during the single point calculation are also statistically significant.

In contrast, the effect of changing the basis set generally does not seem to be statistically significant, comparing across D01, D02, D08, D09 (B3LYP/X/PCM). Comparing across D03, D12, D13 ($\omega$B97X-D3/X/PCM), 6-31G* performed the best with statistically significant improvement, even though it was the smallest basis set tested. This
confirms our statement above that using a larger basis set is not recommended. The effect of using SMD (D14, D15) over PCM is also not statistically significant, again leading us to recommend using PCM, the less computationally expensive solvent model.

5 Conclusions

When calculating the hydricity of organic hydrides, we recommend using \omega B97X-D3 for the density functional, a basis set no larger than TZVP, and PCM as the solvent model. We also generally advise turning PCM off for geometry optimization and frequency analysis calculations, and keeping PCM on for the single point calculations. If the molecule of interest has a net neutral charge, or if one is interested only in the relative hydricities across different molecules with the same charge, then it is safe to turn off PCM for the single point calculations as well.

A future direction of this project is running ab-initio molecular dynamics (AIMD) simulations to study the hydration of solutes in water. Continuum solvent models such as PCM or SMD fail to model strong solvent-solvent and solvent-solute interactions such as hydrogen bonding, so for hydrides in water, a simple DFT calculation with just a continuum solvent will not suffice. A diagnostic algorithm that can determine the importance of certain solvent-solute interactions and give the user a recommendation as to which solvent model to use is also a future direction that would be valuable to theoretical chemistry literature. Such an algorithm could be developed using machine learning approaches.

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