Density Functional Theoretical Study on the Hydricities of (η⁵-C₅H₅)M(CO)₂H (M = Fe, Ru, and Os) in Acetonitrile

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Transition metal hydrides can act as proton donors, hydrogen atom donors, or hydride donors depending on the mode of metal-hydrogen bond cleavage. The acidity is experimentally determined by equilibration with a base. Bond dissociation enthalpy and Gibbs energy are very useful when we predict the reactivity of the metal hydride in hydrogen atom transfer reaction.¹ Hydricity is related to the thermodynamics of the heterolytic dissociation of a hydride anion from the parent molecule,² and has been used to elucidate the reactivity and mechanism of hydride shift reactions³ and hydride abstraction reactions.⁴ The reduction of carbon dioxide by transition metal hydride complexes is a good example of where this concept can be applied.⁵ Although the concept of hydricity parallels that of acidity, an experimental estimation of hydricity requires a series of chemical equations, which is unlike the case of acidity evaluation.⁶ Therefore, the accuracy of the numerical values for hydricity may be affected by errors accumulated from each step. Accordingly, it is important to establish a scheme to calculate the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. We reported a computational scheme for calculating the hydricity from a single step through computation. 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We reported a computational scheme for calculating the hydricity from a single step through calculation.
dynamics results correlate well with the experimental pK_a and bond dissociation thermodynamics. Moreover, inclusion of the solvation energy term gave a similar correlation with better slopes. The hydricities of the complexes are reported based on these results.

### Computational Details

The calculation scheme used for the hydricity evaluation is parallel to that for the pK_a evaluation described earlier.\(^7\)\(^{10}\)

The free energy of deprotonation of HA into its conjugate base A\(^{-}\) is given as

\[
\Delta G_{\text{diss,sol}}^0 = \Delta G_{\text{sol}}^0 (A^{-}) + \Delta G_{\text{sol}}^0 (H^{+}) - \Delta G_{\text{sol}}^0 (AH). \tag{1}
\]

The corresponding pK_a value of HA is given by\(^7\)\(^{10}\)

\[
pK_a = \frac{\Delta G_{\text{diss,sol}}^0}{2.303RT} \tag{2}
\]

Similarly, the hydricity of a molecule AH in a solution is the Gibbs energy of a heterolytic dissociation process, \(\Delta G_{\text{hydricity,sol}}^0\), which is defined as follows (See Scheme 1):

\[
\text{Hydricity} = \Delta G_{\text{hydricity,sol}}^0 = \Delta G_{\text{sol}}^0 (A^{-}) + \Delta G_{\text{sol}}^0 (H^{+}) - \Delta G_{\text{sol}}^0 (AH). \tag{3}
\]

### Table 2. Calculated hydricity values of hydride complexes (unit: kcal mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Hydride complex</th>
<th>Hydricity (sol)</th>
<th>Hydricity (gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(η(^5)-C(_5)H(_5))Fe(CO)(_2)H</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>(η(^5)-C(_5)H(_5))Ru(CO)(_2)H</td>
<td>64</td>
<td>65</td>
</tr>
<tr>
<td>(η(^5)-C(_5)H(_5))Os(CO)(_2)H</td>
<td>78</td>
<td>80</td>
</tr>
<tr>
<td>(η(^5)-C(_5)Me(_5))Fe(CO)(_2)H</td>
<td>55</td>
<td>46</td>
</tr>
<tr>
<td>(η(^5)-C(_5)H(_5))Cr(CO)(_2)H</td>
<td>68</td>
<td>65</td>
</tr>
<tr>
<td>(η(^5)-C(_5)H(_5))Mo(CO)(_2)H</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>(η(^5)-C(_5)Me(_5))Mo(CO)(_2)H</td>
<td>74</td>
<td>74</td>
</tr>
<tr>
<td>(η(^5)-C(_5)Me(_5))Mo(CO)(_2)H</td>
<td>62</td>
<td>52</td>
</tr>
</tbody>
</table>

The standard free energy of each species (AH, A\(^{-}\), and H\(^{+}\)) in a solution, \(\Delta G_{\text{sol}}^0\), can be expressed as the sum of the gas-phase standard free energy, \(\Delta G_{g}^0\), and standard free energy of solvation in water, \(\Delta G_{\text{solv}}^0\):

\[
\Delta G_{\text{sol}}^0 = \Delta G_{g}^0 + \Delta G_{\text{solv}}^0 \tag{4}
\]

The standard free energy of each species in the gas phase, \(\Delta G_{g}^0\), was obtained by
The total energy of the molecule at 0 K ($E_0K$) was calculated at the geometry optimized with quantum mechanics (QM). Harmonic oscillator-rigid rotor approximation was used for the calculation. The zero-point energy (ZPE) and vibrational contribution to the Gibbs energy change from 0 K to 298 K ($\Delta\Delta G_{0 \rightarrow 298K}$) were calculated from the frequencies obtained from the QM calculations. The translational and rotational free energy contribution was also calculated in an ideal gas approximation. ($H - H$) was used as a fitting parameter to ensure the best reproduction of the experimental data, as reported in previous pKa calculations.\textsuperscript{10,11}

All QM calculations were performed using Jaguar v5.5 quantum chemistry software.\textsuperscript{12} The B3LYP\textsuperscript{13-16} variation of DFT for geometry optimization and to calculate the energies of the molecules. Since calculations of the vibration frequencies are generally time-consuming, a small basis set of the LACVP** basis set was used to optimize the geometry and calculate the vibration frequencies. The number of imaginary frequencies was monitored to determine if the optimized structure of each chemical species corresponds to the true minimum. The Poisson-Boltzmann continuum model\textsuperscript{17,18} was used to describe the solvent (acetonitrile) at the B3LYP/LACVP** level. The solvent probe radius was 2.18 Å, and the solvent dielectric constant was 35.69, as reported previously.\textsuperscript{19}

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References