Density Functional Theoretical Study on the Hydricities of (η^5-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 reactions[3] 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.[2] 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 in an aqueous solution.[6] Recently, Estes and coworkers estimate the pK_a values, bond dissociation Gibbs energies, and hydricities of (η^5-C₅H₅)M(CO)₂H (M = Fe, Ru, and Os) in acetonitrile.[1]

In the present study, density functional theoretical (DFT) calculations of these transition metal hydrides were performed and the results were compared with the experimental data. The pK_a values, which show the acidity of hydride complexes, were calculated. Table 1 lists the chemical structures of the metal complexes used in this study, along with the calculated pK_a values and experimental estimation.

First the pK_a of the complexes was compared with the theoretical estimation based on the Gibbs energy for the dissociation of protons in the gas phase, $\Delta G^0_{\text{diss,gas}}$. The Gibbs energy of a proton in the gas phase, $\Delta G^0_{\text{gas}}(\text{H}^+)$, was used as a fitting parameter to obtain the best correlation. Figure 1 shows the pK_a of the 8 molecules against the theoretical values listed in Table 1. Gas phase dissociation showed good agreement with the experimental data (R^2 = 0.99) with a slope of 1.39. Taking the solvation energy into consideration gave a similar correlation (R^2 = 0.98) with a slope of 1.12. Unlike the case of an aqueous solution,[6] the

Table 1. Experimental and calculated pK_a of the hydride complexes examined in this study

| Hydride complex | pK_a | | | |
	exp[a]	calc (sol)[b]	fitted[c]	calc (gas)[d]
1 (η^5-C₅H₅)Fe(CO)₂H	27.1	30.5	27.2	38.9
2 (η^5-C₅H₅)Ru(CO)₂H	28.3	29.6	26.5	37.9
3 (η^5-C₅H₅)Os(CO)₂H	32.7	36.6	32.2	46.0
4 (η^5-C₅Me₅)Fe(CO)₂H	29.7	35.7	31.9	41.1
5 (η^5-C₅H₅)Cr(CO)₂H	13.3	15.5	13.8	19.8
6 (η^5-C₅H₅)Mo(CO)₂H	13.9	15.1	13.5	19.2
7 (η^5-C₅H₅)W(CO)₂H	16.1	18.0	16.1	23.1
8 (η^5-C₅Me₅)Mo(CO)₂H	17.1	19.0	17.0	22.5

[a]reference. [b]from the calculated results using B3LYP/LACVP** including the solvation energy calculations. [c]fitted with the correlation result. [d]from the calculated results using B3LYP/LACVP** with gas phase calculations

result shows that the solvation energy calculation is not essential for making an accurate pK_a evaluation. On the other hand, inclusion of the solvation energy calculation gave values with a slope of approximately 1.0. Calculations with an additional solvent as a weakly bound ligand (or as the simplest model of the explicit solvent model) did not improve the quality of the correlation, which is unlike the case of an aqueous solution.[6]

Figure 2 presents the calculated the Gibbs energy of M–H bond dissociation. Similar to the pK_a calculation, inclusion of the solvation energy did not affect the correlation. As in the case of pK_a calculations, calculations with an additional solvent as a weakly bound ligand did not improve the quality of the correlation unlike the case of an aqueous solution.[6]

Table 2 presents the hydricity values estimated from the calculations. $\Delta G^0_{\text{sol}}(\text{H}^-)$ was used as a fitting parameter to obtain the best fit to the experimental data for (η^5-C₅H₅)-Fe(CO)₂H (62 kcal mol⁻¹). Only the calculated values are tabulated because only the hydricity of one species is reported.

In summary, B3LYP variation of DFT calculations coupled with a Poisson–Boltzmann continuum solvent model were performed to calculate the hydricities of transition metal hydrides in acetonitrile. The computation scheme is parallel to the pK_a calculations. The gas phase thermo-
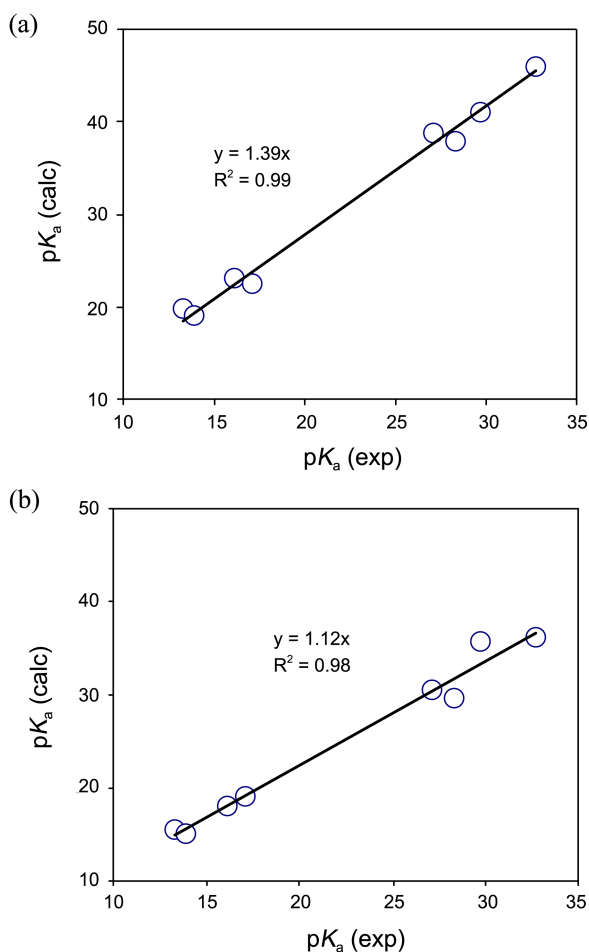
Figure 1. pK_a of the transition metal hydride complexes (a) from gas-phase calculations and (b) with solvation energy calculations.

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 eariler.[7-10] The free energy of deprotonation of HA into its conjugate base A^- is given as

$$\Delta G^0_{\mathrm{diss,sol}} = \Delta G^0_{\mathrm{sol}}(A^-) + \Delta G^0_{\mathrm{sol}}(H^+) - \Delta G^0_{\mathrm{sol}}(AH). \quad (1)$$

The corresponding pK_a value of HA is given by[7-10]

$$pK_a = \Delta G^0_{\mathrm{diss,sol}}/2.303RT \quad (2)$$

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

$$\mathrm{Hydricity} = \Delta G^0_{\mathrm{hydricity,sol}} = \Delta G^0_{\mathrm{sol}}(A^+) + \Delta G^0_{\mathrm{sol}}(H^-)$$
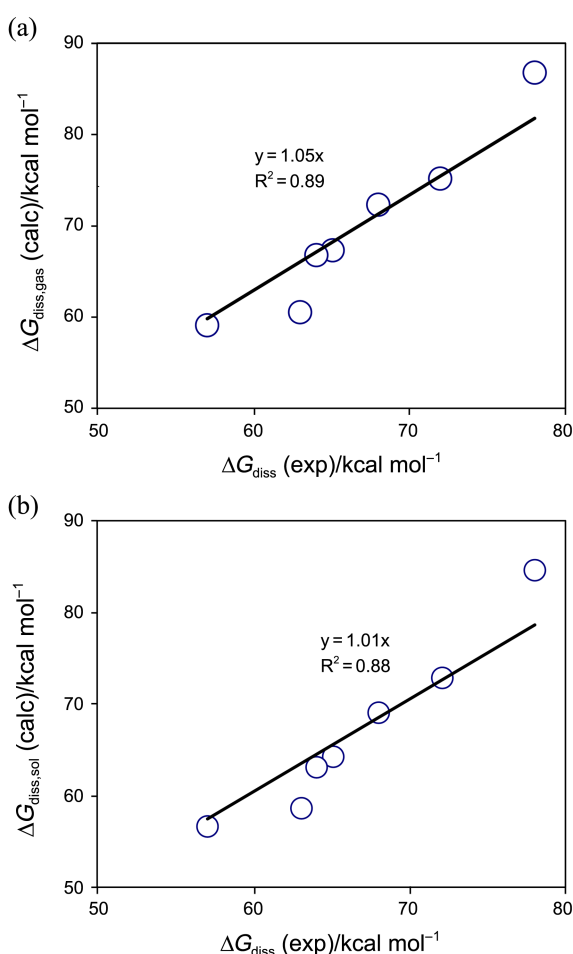$$- \Delta G^0_{\mathrm{sol}}(AH). \quad (3)$$

Figure 2. Gibbs energy of M–H bond dissociation of transition metal hydride complexes, (a) from gas phase calculations and (b) with solvation energy calculations.

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

	Hydride complex	Hydricity (sol)	Hydricity (gas)
1	(η^5-C$_5$H$_5$)Fe(CO)$_2$H	62	62
2	(η^5-C$_5$H$_5$)Ru(CO)$_2$H	64	65
3	(η^5-C$_5$H$_5$)Os(CO)$_2$H	78	80
4	(η^5-C$_5$Me$_5$)Fe(CO)$_2$H	55	46
5	(η^5-C$_5$H$_5$)Cr(CO)$_2$H	68	65
6	(η^5-C$_5$H$_5$)Mo(CO)$_2$H	67	67
7	(η^5-C$_5$H$_5$)W(CO)$_2$H	74	74
8	(η^5-C$_5$Me$_5$)Mo(CO)$_2$H	62	52

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

$$\Delta G^0_{\mathrm{sol}} = \Delta G^0_{\mathrm{g}} + \Delta G^0_{\mathrm{solv}} \quad (4)$$

The standard free energy of each species in the gas phase, ΔG^0_{g}, was obtained by
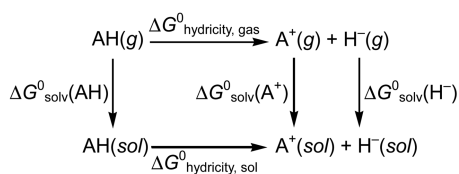
Scheme 1. Thermodynamic cycle used to calculate the hydricity values.

$$\Delta G_g^0 = E_{0K} + ZPE + \Delta\Delta G_{0\rightarrow 298K}. \tag{5}$$

The total energy of the molecule at 0 K ($E_{0\,K}$) 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 ($\Delta\Delta G_{0\rightarrow 298\,K}$) 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. ΔG_{aq}^0 (H⁻) was used as a fitting parameter to ensure the best reproduction of the experimental data, as reported in previous pK_a calcuations.[10,11]

All QM calculations were performed using Jaguar v5.5 quantum chemistry software.[12] The B3LYP[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 Poison-Boltzmann continuum model[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.[19]

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