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Hydricities of d^6 Metal Hydride Complexes in Water

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The concept of hydricity parallels that of acidity; hydricity is related to the thermodynamics of heterolytic dissociation of hydride anion from parent compound D-H, *i.e.*, (1-1) in Scheme 1. Experimental estimates of hydricity are obtained from cycles based on combinations of the processes in Scheme 1. Parker and DuBois determined hydricity (1-1) from the free-energy changes for (1-2), (1-4), (1-5), and (1-6) as $\Delta G^o_{H^-} = \Delta G^o_{H^+} - 2\,E^o(D^+/D^-) + \Delta G^o_{H^+}(H_2) + 2E^o(NHE)$ for bonds between H and nonmetals and transition metals, respectively, in organic solvents.[1−4] Although water is recognized as a desirable solvent for catalysis[5,6] and as a promising raw material for solar generation of fuels such as H_2 and CH_3OH (from CO_2 and water),[7] relatively few kinetics and equilibrium studies of hydricity in aqueous media have been reported.[6,8] For a number of cobalt(III) and rhodium(III) complexes, hydricities in water may be evaluated from the cycle used above. Two estimates of the acidity of H_2, differing by 9.5 pK units, have been given: 31.5[9] and 22.[10] Here, values derived from the older (and very widely used value, 31.5) are used to facilitate comparison with other data sets. In water $E^o(NHE) = 0$. Representative data are shown in Figure 1 (cf. Table S1) in which the uncertainties are roughly indicated by the size of the data markers. The data for the cationic complexes all fall near the line of slope 1.0. The dashed line indicates the hydricity of HCO_2^-. Complexes lying below the line are thermodynamically capable of CO_2 reduction to formate.

Scheme 1

(1-1) Hydricity	$D\text{-}H = D^+ + H^-$	$\Delta G^o_{H^-}$
(1-2) Acidity	$D\text{-}H = D^- + H^+$	$\Delta G^o_{H^+}(H_2)$, pK_a
(1-3) Homolysis	$D\text{-}H = D + H\bullet$	$\Delta G^o_{H\bullet}$
(1-4) Reduction	$D^+ + 2e^- = D^-$	$E^o(D^+/D^-)$
(1-5) H_2 Acidity	$H_2 = H^- + H^+$	$\Delta G^o_{H^+}$, pK_a
(1-6) NHE	$2H^+ + 2e^- = H_2$	$E^o(NHE)$

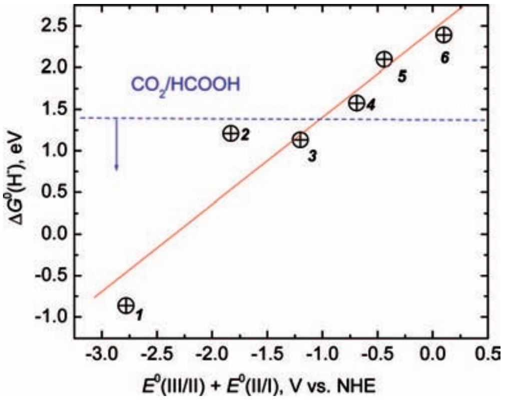


Figure 1. The numbered points are as follows: $CoCp_2H$ (**1**), $Co(CN)_5H^{3-}$ (**2**), $RhCp^*(bpy)H^+$ (**3**), $Co(bpy)_2H(H_2O)^{2+}$ (**4**), $Co(HMD)H(H_2O)^{2+}$ (**5**), $Rh(bpy)_2H(H_2O)^{2+}$ (**6**) (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). See Table S1; based on $pK(H_2) = 31.5$.

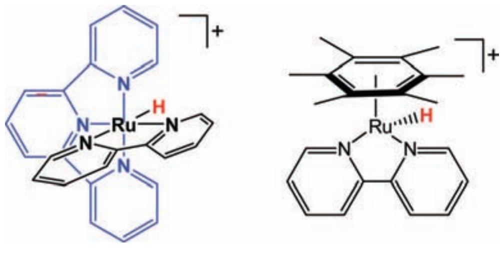
Figure 1 includes data for d^6 metal hydrides for which pK_a's are known because of the accessibility of the corresponding d^8 M^I base. An alternative approach is needed for poorly acidic d^6 hydrides. A number of Ru(II) complexes serve as transfer hydrogenation catalysts using formate as a hydrogen source and/or catalyze the hydrogenation of CO_2 to HCO_2^-,[11−19] suggesting the possibility of using equilibration with the CO_2/HCO_2^- couple (Scheme 2) to establish the hydricities of metal−hydride complexes in water. The complexes studied are shown in Chart 1.

Scheme 2. Equilibration of Hydride Complex, CO_2, and HCO_2^-

$$Ru(H_2O)^{2+} + HCO_2^- \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} Ru(HCO_2)^+ \underset{k_{-B}}{\overset{k_B}{\rightleftharpoons}} RuH^+ + CO_2 \qquad (2\text{-}1)$$

$$K_{AB} = \frac{[RuH^+][CO_2]}{[Ru(H_2O)^{2+}][HCO_2^-]} = K_A K_B = \frac{k_A k_B}{k_{-A}k_{-B}} \qquad (2\text{-}2)$$

Chart 1



As shown for ***2***(H) in Figure 2, both ***1***(H) and ***2***(H) react with CO_2 in water to yield formate ion.[19−21] Spectral changes and the CO_2 concentration dependence are also shown in Figure S2 and Table S2. Fits to the data are shown in Figure S3.

The occurrence of the reverse reaction of the aquo complex ***2*****(H_2O)** with HCO_2^- to yield ***2***(H) (Scheme 2) has been reported at higher temperature[20] and is also evident at room temperature (compare Figures 2 and 3). Although the kinetics of the approach to equilibrium in Scheme 2 can be extremely complex,[22] the stages corresponding to HCO_2^- binding (k_A, k_{-A}) could be resolved at moderate HCO_2^- concentration (Figure S4) and verified by comparison with binding by an acetate ion (Figures S5−S7), by independently measuring the loss of HCO_2^- ion from a sample of the complex isolated as a solid (Figures S8−S9) and by comparisons with stochastic simulations[23] (Figure S10). Values of k_{-B} and k_A were determined from the slopes of the inserts in Figures 2 and 3, respectively. Values are summarized in Table 1 (estimated errors ± 15% of tabulated value unless otherwise noted). The Ru(terpy)(bpy) substitution equilibrium was studied analogously. However, because of the instability of the hydride complex on the time scale required for its formation by k_B, we instead analyzed H_2 obtained over 72 h to estimate k_B.

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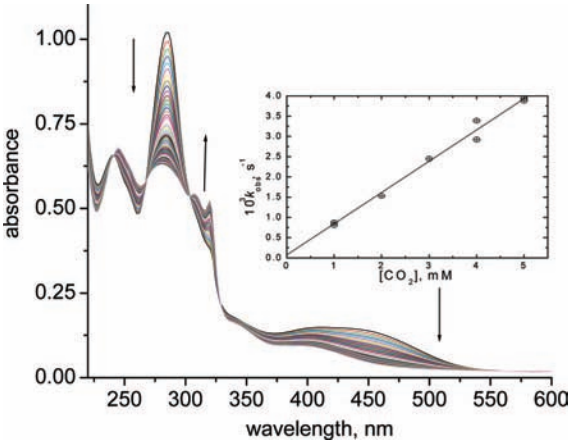

Figure 2. UV−vis changes for reaction of Ru(η^6-C_6Me_6)(bpy)H(TFMS) (0.1 mM) with 2 mM CO_2 at ionic strength 0.5 M (Na_2SO_4) at 25 °C every 45 s. Inset: Pseudo-first-order rate constants for 454 nm vs [CO_2].

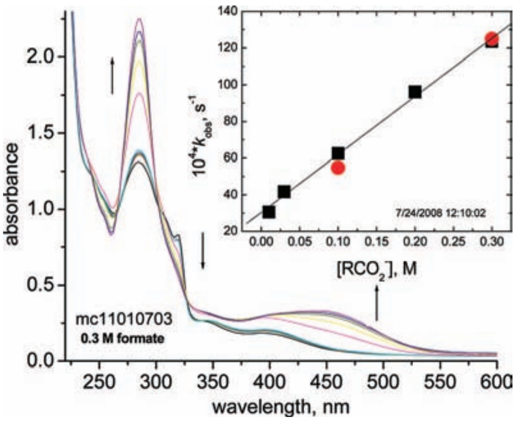

Figure 3. UV−vis changes for reaction of ***2***-H with 0.3 M HCO_2^- at ionic strength 0.5 M (Na_2SO_4) at 25 °C. Inset: k_{obs} for the binding of RCO_2^-: acetate (black squares) and formate (red circles).

Table 1. Rate and Equilibrium Constants for Scheme 2

	quantity	Ru(terpy)(bpy)H$^+$	Ru(η^6-C_6Me_6)(bpy)(H)$^+$
i	k_A, M^{-1} s^{-1}	3×10^{-4a}	3.2×10^{-2a}
ii	k_{-A}, s^{-1}	2×10^{-4a}	$(3 \pm 1) \times 10^{-3a}$
iii	$K_A = k_A / k_{-A}$ M^{-1}	1.5^c	11^c
iv	k_{-B}, M^{-1} s^{-1}	8.5×10^{2b}	0.77^a
v	k_B, s^{-1}	$(5 \pm 1.5) \times 10^{-7a,d}$	0.91×10^{-4a}
vi	$K_B = k_B/k_{-B}$, M	5.9×10^{-10e}	1.3×10^{-4e}
vii	$K_AK_B = K_{AB}$	0.9×10^{-9f}	1.4×10^{-3f}
viii	$\Delta G_{AB}{}^{\circ}$, kcal/mol	12.2^a	3.9^a

[a] This study. [b] As reported earlier.[19] [c] From the rate constant ratio entry *i* divided by *ii*. [d] Determined by comparing the number of moles of H_2 produced per Ru over a 72 h period with that produced from RuH and the phosphate buffer. [e] Obtained by dividing entry *iv* by *v*. [f] The product of *iii* and *vi*.

For CO_2 reduction, processes (1-4), (1-5), and (1-6) were used[19] to obtain $\Delta G°_{H^-}(HCO_2^-) = +34.8$ kcal/mol. Hydricities of +22 and +31 kcal/mol are then derived for ***1***(H) and **2**(H), respectively. These values, 0.96 and 1.35 eV, thus bracket that of Rh(*Cp)(bpy)H$^+$, 1.13 eV, which exhibits similar chemistry[24,25] and for which the value of k_B is ca. 40 times greater than that for ***2***.[26]

The equilibrium constant K_A for replacement of the aquo ligand by formate ion is <10 times greater for ***2***(H_2O) than for ***1***(H_2O); however K_{AB} for the overall transformation to ***1***(H) and CO_2 is $>10^6$ more favorable than that for ***2***(H_2O). Examination of step B, -B in Scheme 2 reveals that $k_B(\mathbf{1})/k_B(\mathbf{2}) = 2 \times 10^3$, $k_{-B}(\mathbf{2})/k_{-B}(\mathbf{1}) = 1.1 \times 10^3$. Thus both forward and reverse rate constants scale by the square root of the equilibrium constant. Future studies will focus on the generality and significance of this correlation.

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Supporting Information Available: Experimental details, kinetics, and products for reaction with CO_2 and HCO_2^-, the hydricities of metal hydride complexes ***1***−***6***. This material is available free of charge via the Internet at http://pubs.acs.org.

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