The Reaction of Cobaloximes with Hydrogen: Products and Thermodynamics

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Supporting Information Placeholder

ABSTRACT: A cobalt hydride has been proposed as an intermediate in many reactions of the $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$ system, but its observation has proven difficult. We have observed the UV-vis spectra of $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$ (**1**) in CH_3CN under hydrogen pressures up to 70 atm. A $\text{Co}(\text{I})$ compound (**6**), with an exchangeable proton, is eventually formed. We have determined the bond dissociation free energy and $\text{p}K_{\text{a}}$ of the new O–H bond in **6** to be 50.5 kcal/mol and 13.4, respectively, in CH_3CN , matching previous reports.

In addition to being functional B_{12} models¹ and catalyzing the production of hydrogen from protons and electricity,² cobaloximes catalyze $\text{H}\cdot$ transfer from H_2 .³ $\text{Co}(\text{dmgBF}_2)_2\text{L}_2$ (**1**) and $\text{Co}(\text{dmgH})_2\text{L}_2$ (**2**) (dmg = dimethylglyoximate; $\text{L} = \text{H}_2\text{O}$, CH_3CN , etc.) can, under H_2 , transfer $\text{H}\cdot$ to stable radicals such as TEMPO (Scheme 1)⁴ and generate radicals by $\text{H}\cdot$ transfer to activated alkenes⁴ and alkynes.⁵ The cobaloxime **1** can thus generate radicals from α -substituted acrylate esters, and catalyze radical cyclohydrogenation reactions.⁴ The reaction of **1**, H_2 gas, and TEMPO is independent of $[\text{TEMPO}]$, first order in H_2 , and second order in **1**, suggesting that its rate-determining step involves an H_2 and two equiv of **1** (the forward reaction of eq 1).⁴

When **1** and **2** catalyze the production of H_2 from protons (Scheme 2),^{2a, b, 6} cobaloxime hydrides **3** have been proposed as key intermediates, although they have never been directly observed. Little is known about their structure, spectroscopy, and reactivity.

Scheme 1. Hydrogen atom transfer (HAT) from H_2 to stable free radicals ($\text{X}\cdot = \cdot\text{CAR}_3$ or TEMPO) catalyzed by **1**

We have therefore attempted to determine the spectroscopic and thermodynamic properties (i.e. the $\text{p}K_{\text{a}}$, the bond dissociation free energy (BDFE), etc.) of the hydrides of **1** in various solvents. In this paper, we report the behavior of **1** under relatively high hydrogen pressures (70 atm) and use our findings to assess other observations in the literature about the 1/H_2 system.

Scheme 2. Electrocatalytic production of H_2 with **1**

When **1c** is dissolved in CH_3CN it gives complex **1a**,^{6c, 7} with λ_{max} at 434 nm ($3240 \text{ M}^{-1}\text{cm}^{-1}$). Under 70 atm of H_2 at room temperature its UV-vis spectrum changes slowly (24 h) but smoothly (Figure 1) into one with a λ_{max} at 556 nm ($7700 \text{ M}^{-1}\text{cm}^{-1}$), another at 627 nm ($7460 \text{ M}^{-1}\text{cm}^{-1}$), and a small peak at 354 nm. The process is reversible; the original spectrum returns slowly (48 h) after release of the gas pressure.

Figure 1. UV/vis difference spectra recorded over the course of 24 h for complex **1a** in CH₃CN, pressurized with 70 atm of H₂ gas at room temperature.

We previously determined that the reaction of **1a** with H₂ is termolecular, with the hydride **3a** as the presumed product.⁴ We have now quantified the **1a**/H₂ equilibrium with the Benesi–Hildebrand method, modified for a ternary equilibrium like that in eqs 2–4 (see the Supporting Information for derivation).⁸ By varying the hydrogen pressure and fitting the absorbance data to eq 4 (Figure 2) we obtain a $\Delta\epsilon$ of 785 M⁻¹ cm⁻¹ and an equilibrium constant (K_{eq})⁹ of 0.014(7) atm⁻¹.

$$K_{eq}(\text{atm}^{-1}) = \frac{[{}^{\prime}\text{Co-H}]^2}{[1a]^2 P_{H_2}} \quad (3)$$

We can use this value of K_{eq} to estimate a $\Delta G_{rxn} = 2.5(3)$ kcal/mol for eq 2. Use of the bond dissociation free energy (BDFE) of H₂ (103.6 kcal/mol)¹⁰ with eq 6 gives the free energy change of eq 5, $\Delta G_H = 50.5(3)$ kcal/mol.¹⁰

Figure 2. Plot of $P_{H_2}^{-1}$ vs the inverse of the change in absorbance of **1a** at 434 nm $(A-A_0)^{-1}$, measured in CH₃CN under different H₂ pressures. The blue curve is a fit of the data to eq 4.

From the thermodynamic cycle in eq 7¹⁰ we can estimate the pK_a of the product as 13.4 in CH₃CN using the ΔG_H from above and the potential of the Co(I)/Co(II) couple (-0.93 V vs Fc/Fc⁺).^{6d} Artero and Fontecave observed that the protona-

tion of **5a** during H₂ evolution occurred with a pK_a of 13.3, in good agreement with our estimate.^{6d} This pK_a is consistent with the facts that (a) proton transfer from HNEt₃⁺ ($pK_a = 18.8$)¹¹ to **5b** is slow and unfavorable (still incomplete after 8 s, Figures S11 and S12), and (b) catalysis of hydrogen evolution by **1a** does not occur with acids weaker than HNEt₃⁺.

$$\frac{1}{P_{H_2}} = K_{eq} \left(\frac{[1a]_0^2 \Delta\epsilon^2 \left(\frac{1}{A-A_0} \right)^2}{-2[1a]_0 \Delta\epsilon \left(\frac{1}{A-A_0} \right) + 1} \right) \quad (4)$$

$$\Delta G_H = \Delta G(H-H) - 2\Delta G_7 \quad (6)$$

$$BDFE = 1.37pK_a + 23.06E_{ox}^0 + 53.6 \frac{\text{kcal}}{\text{mol}} \quad (7)$$

In order to characterize the product of reaction 2, we monitored the ¹H NMR spectrum of **1a** in CD₃CN under 70 atm of H₂. No signal that could be attributed to Co–H was observed, as far upfield as $\delta = -25$ ppm (see Figure S8). Of course, residual coupling to the ⁵⁹Co could broaden the hydride signal and make it difficult to observe. We did see a new resonance (see Figure 3, the full spectrum is in Figure S8) at δ 2.06 ppm and a new broad peak at δ 2.50 ppm.¹² The peak at δ 2.50 ppm disappeared when the pressure was released. In the presence of exchangeable D⁺, as in CD₃OD, the δ 2.50 ppm signal does not appear (Figure S9), suggesting that it belongs to an exchangeable proton. Both **1a** and **2a** catalyze H/D exchange between D₂ and H₂O (¹H NMR in Figure S5, ²H NMR in Figure S6).

6i

Figure 3. ¹H NMR spectra of **1a** in CD₃CN under 1 atm of argon (black) and 70 atm of H₂ (red) (*CHD₂CN)

Thus the product of the reaction of **1a** with H₂ may not be the cobalt hydride **3a**. That hydride is probably the first species observed by Dempsey and Gray after protonation of the anion **5a** with a photoacid⁶ⁱ — a species with a high absorb-

ance at 405 nm. However, as Figure 1 shows, the reaction of **1a** with H₂ gives a species (**6a**) with little absorbance at 405 nm but peaks at 556 and 627 nm — a spectrum similar to that of the electrochemically generated Co(I) anion **5a** (Figure 4, top).

Figure 4. Spectroelectrochemistry of the reduction of **1a** in CH₃CN (top) and **1b** in THF (bottom) at an applied potential of −1.0 V vs Ag wire. Solutions contain 0.1 M NBu₄BF₄ as an electrolyte.

One possible structure for **6a** — which includes a Co(I) and an exchangeable proton — is drawn in eq 8 below. A similar structure has been suggested by Artero and Fontecave for the mischaracterized “HCo(dmgH)₂PBu₃”.^{4,13} The fact that no hydride resonance is observed during reaction 2 in CH₃CN suggests that H₂ activation is rate determining in the formation of **6a** from **1a** and H₂, a conclusion supported by measurements of the rate at which **1a** reacts with H₂.⁷

The structure drawn for **6a** would have four inequivalent methyls, although we observe only one peak (the one at δ 2.06 ppm) in the ¹H NMR that can be so assigned. However, it is possible that the proton causing the inequivalence could undergo a proton-coupled electron transfer (PCET) from **6a** to **1a** in solution, causing the methyl groups to exchange with each other on the NMR time scale (Scheme 3). This would produce a spectrum with only one methyl peak. When we lower the temperature of the pressurized sample (Figure S10), the pressure of H₂, and thus the amount of H₂ dissolved in the solution, decreases (as indicated by the intensity of the

free H₂ peak in the NMR), and the chemical shift of the supposed methyl signal at 2.06 ppm increases. This presumably increases the ratio of **1a** to **6a** in solution, causing simultaneous broadening and shifting of the methyl resonance while the position and shape of the proton at 2.5 ppm remains the same.

Scheme 3. Possible mechanism of PCET between **6a** and **1a**.

We also monitored the UV-vis spectrum of a solution of Co(dmgBF₂)₂(THF)₂ (**1b**) under 70 atm H₂ in THF (Figure 5). Over the course of 8 h we observed bleaching of the signal at 430 nm in conjunction with the appearance of new peaks at 354 and 305 nm. After 8 h, a third species grew in at 580 nm, as the 354 nm absorbance decreased.

Figure 5. UV-vis difference spectra recorded over the course of 24 h for complex **1b** in THF pressurized with 70 atm of H₂ gas at room temperature.

The absorbance of the intermediate in THF (354 nm) is similar to that observed for Co(dmgBF₂)₂(CH₃CN)Me,⁶ⁱ similar to the spectrum calculated for **3a**,¹⁴ and similar to the absorbance observed by Dempsey and Gray which they attributed to **3**.⁶ⁱ We believe that in THF the intermediate at 354 nm is the hydride complex **3b** — presumably the initial product of the termolecular reaction with hydrogen.¹⁵ We have not been able to look for a hydride resonance in the NMR spectra in THF because of the low solubility of **1b** in that solvent. The subsequent 580 nm absorbance may be due to a tautomerized product, similar to **6a**. This 580 nm peak is shifted relative to the 630 nm peak seen for the Co(I) anion **5b** (Figure 4, bottom). This could be the result of different populations of the open and closed forms of **6b** shown in Scheme 3. Changing the

axial ligand from CH₃CN to THF may change the p*K*_a of the hydride (**3**) enough to slow down its tautomerization.

A tautomerized product, like **6a**, could explain some observations in the hydrogen evolution literature that were originally attributed to hydride **3a**. Compound **6** may be the kinetic product of protonation of **5**. Upon rapid mixing of **5c** with acid, Bakac and co-workers observed an intermediate with λ_{max} at 610 nm, similar to that of **5c** but less intense ($10^4 \text{ M}^{-1}\text{cm}^{-1}$).^{6f} They attributed this feature to the hydride **3c**, but given the spectrum observed for the hydride **3a** by Dempsey and Gray (high absorbance at 405 nm), we question this assignment, and propose that the Bakac spectrum may be due to the ligand-protonated complex **6c** (the spectra are quite similar). However, during the photochemical protonation of **5a**, Gray and coworkers observed direct protonation of the metal.⁶ⁱ Bakac's experiment was done with excess citrate present, which could coordinate to the boron and make the ligand's oxygen available for protonation. The citrate could also catalyze the proton transfer necessary for the conversion of **6a** to **3a**, in the way Bullock and DuBois observe for [Ni(P₂N)₂]²⁺ complexes.¹⁶

In summary, in CH₃CN under large pressures of H₂, cobaloxime **1a** is converted to a product, **6a**, having a Co(I) center and an exchangeable proton, which is possibly a tautomer of the hydride **3a**. In THF, however, the major product under high hydrogen pressures may well be the hydride **3b**. This difference in reactivity is most likely due to the hydride **3b** being less acidic than **3a**. The free energy of H• donation and the p*K*_a of **6a** are 50.5 kcal/mol and 13.4, respectively. However, the assignment of the position of the proton on the ligand cannot conclusively be determined from the data presented.

It is possible that the same hydride tautomer is an intermediate in the mechanism of electrocatalytic hydrogen gas production by cobaloximes. It may be the cause of the difficulty in characterizing cobaloxime hydrides in these reactions.

ASSOCIATED CONTENT

Supporting Information

Experimental detail, NMR data, UV-vis data, derivation of eq 6, stopped flow data.

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The authors declare no competing financial interests.

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12. The extremely large absorbance of H₂ in the NMR spectrum causes truncation errors in the FID of these spectra. This produces a "rippling" effect radiating from the edges of the H₂ peak. This causes large errors in the integral of the broad peak at 2.50 ppm and thus the ratio of the peak at 2.5 ppm to that at 2.06 ppm, with observed ratios being between 1:4 and 1:15. The spectrum with the least H₂ (at 243 K) had the least truncation error and with the integral of the peak at 2.50 ppm being 0.82.

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