Kinetics of Hydride Transfer from Metal-Free Hydride Donors to CO₂

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ABSTRACT: Selective reduction of CO_2 to formate represents an ongoing challenge in photoelectrocatalysis. To provide mechanistic insights, we investigate the kinetics of hydride transfer (HT) from a series of metal-free hydride donors to CO_2. The observed dependence of experimental and calculated HT barriers on the thermodynamic driving force was modeled using the Marcus hydride transfer formalism to obtain the insights into the effect of reorganization energies on the reaction kinetics. Our results indicate that, even if the most ideal hydride donor were discovered, the HT to CO_2 would exhibit sluggish kinetics (less than 100 turnovers at 0.1 eV driving force), indicating that the conventional HT may not be an appropriate mechanism for Solar conversion of CO_2 to formate. We propose that the conventional HT mechanism should not be considered for CO_2 reduction catalysis and argue that the orthogonal HT mechanism, previously proposed to address thermodynamic limitations of this reaction, may also lead to lower kinetic barriers for CO_2 reduction to formate.

The conversion of CO_2 to value-added products is a promising approach to mitigate the effect of increasing levels of CO_2 in the atmosphere. The two-electron proton-coupled reduction of CO_2 to formic acid represents an attractive transformation because the product can serve as a fuel with high volumetric energy density, easy handling, and low toxicity, or as a reagent in pharmaceutical industry and other synthesis applications.[1,2] However, the selective reduction of CO_2 to formate remains a challenge, and most transition metals catalyze the competing reactions, such as formation of CO and/or H_2[3–8] Only a handful of well-defined molecular catalysts, have been shown to lead to the selective formate formation.[9–17] The product selectivity is generally controlled by either the thermodynamics or kinetics of the reaction between reduced metal and available substrates, namely protons and CO_2.[14,18–21]

In natural photosynthesis, CO_2 is first captured from air and converted to 1,3-bisphosphoglycerate, which is then reduced via the hydride transfer (HT) from the NADPH cofactor.[22] Following in nature's footsteps, our group recently developed hydrides that mimic NADPH activity, and that are sufficiently hydridic to perform a direct reduction of CO_2.[23–28] Our work has shown how the thermodynamic hydricities of metal-free hydrides can be tuned using aromatization, delocalization and hyperconjugation mechanisms and that the benzoimidazole-based hydride C4H (Figure 1) can efficiently reduce CO_2 to formate via the HT mechanism.[26] We also demonstrated that the benzoimidazole-based hydrides can be efficiently regenerated electrochemically by optimizing the conditions for proton-coupled electron transfer, reporting the first proof-of-principle demonstration toward metal-free and selective CO_2 reduction catalysis.[24,27] Despite the successful demonstration of HT to CO_2, the kinetics of the transformation were quite slow in our studies, on the timescale of several hours.

Herein, we report the results of our investigation of the factors that controlling the kinetics of HT from metal-free hydrides to CO_2 by determining, both experimentally and computationally, the HT barriers of the series of hydride donors shown in Figure 1. As expected, our studies reveal that HT kinetics are improved by increasing the thermodynamic driving force of the reaction. The experimental data were
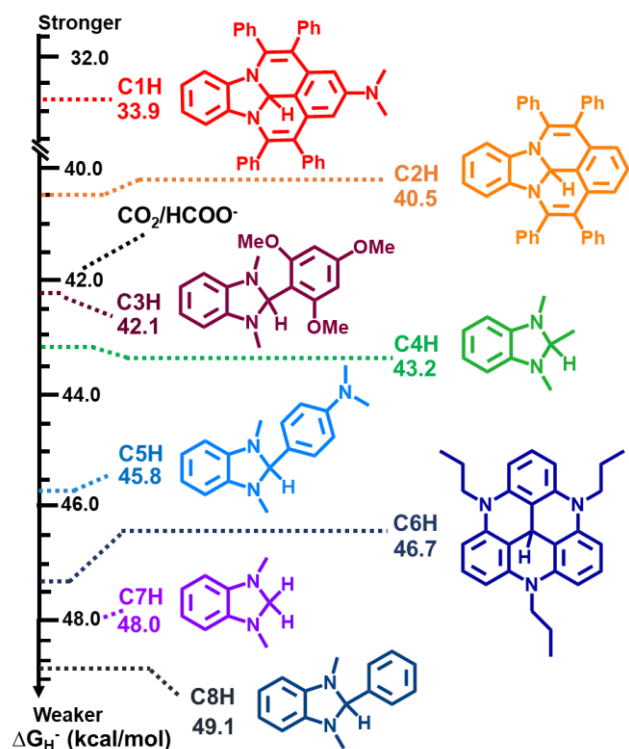
Figure 1. Structures and thermodynamic hydricities of hydride donors in DMSO. The hydricities were calculated at the wB97x-D 6-311+G(d,p) level of theory (computational details are provided in SI, Section S2). The hydricity of formate was obtained from literature.[29]

fit to the Marcus hydride transfer model to obtain the relevant self-exchange reorganization energies of the metal-free hydrides and CO_2/HCO_2^- couple. Our results show that the self-exchange reorganization energies of metal-free hydrides are relatively large (91 kcal/mol), indicating that the appropriate modification of the hydride donor structure yield lower reorganization energies and improved kinetics for HT. However, we find that, even if optimal hydride donors were used, the HT to CO_2 would still be relatively slow, due to the large self-exchange reorganization energy associated with the CO_2/HCO_2^- couple (41 kcal/mol). Our results provide an explanation for why the formate ion is a rarely observed product in electrocatalytic CO_2 reduction and point to possible approaches that can be used to circumvent the limitations of direct HT mechanism.

The synthesis and characterization of model compounds C1H to C8H is described in SI, Section S1. The driving force for HT from organic hydrides to CO_2 was evaluated as the difference between the thermodynamic hydricities (ΔG_{H^-}) of organic hydrides and of formate ((ΔG_{H^-} = 42 kcal/mol[29]) in DMSO. The ΔG_{H^-} values for organic hydrides were calculated using the DFT methodology that was previously shown to agree with experimental values[24] (See SI, Section S2, for computational details). Our results indicate that the strength of hydride donors can be improved in structures where the benzoimidazole and aryl moieties are co-planar (C1H and C2H) or by introducing electron-donating amino and methoxy groups (C1H, C3H, C5H). Overall, the driving force for HT from these hydrides to CO_2 varies between -11 to +5 kcal/mol range (Table S2, SI). The HT driving forces are close to $\Delta G=0$, which is the optimal range for applications in electrocatalysis (if ΔG values were more negative, HT kinetics would likely improve, but the electrochemical regeneration of the hydride would require larger overpotentials).[27,28]

Experimental reaction conditions were tested for CO_2 reduction by organo-hydrides to maximize the formate yield with respect to temperature, pressure, and solvent (SI, Section S1C). Optimal formate production was achieved at high temperatures (100° C), mild CO_2 pressure (~2.2 atm) and in a polar medium (obtained by adding potassium salts to DMSO). An increase in the temperature lead to an increase in formate yields (Figure S1) consistent with the large kinetic barrier associated with HT. The increased polarity of the medium, either by solvents with higher dielectric constant[30,31] (SI, Figures S2 and S3) or by adding alkali and alkaline salts (Figure S4) leads to an increased in formate yields, as expected for a reaction that produced charged products from neutral reactants.[26,32,33] In all reactions, the loss of organic hydride reactants was higher than the growth of formate product (blue and red traces in Figures S1-S5), indicating additional reaction pathways that organic hydrides undergo. While the detailed investigation of this side reaction was not performed, we hypothesize that it involves the reduction of DMSO to DMS, based on the observed NMR peak at 2.01 ppm (Figure S6). Additionally, the calculated reaction free energy between DMSO and organo-hydrides were found to be extremely favorable (See Section S2.B, SI), further confirming that the side reaction may involve DMSO reduction.

We next analyzed the kinetics of HT reactions using organo-hydrides at the optimized conditions using ^{1}H-NMR spectroscopy. Figure 2 illustrated the kinetic analysis for C4H, while the results for other hydrides are shown in Table S2 and Figures S7-S14, SI. Peaks associated with the hydride donor C4H (at 6.52 and 6.35 ppm) were found to decrease in intensity, while a concomitant increase in the
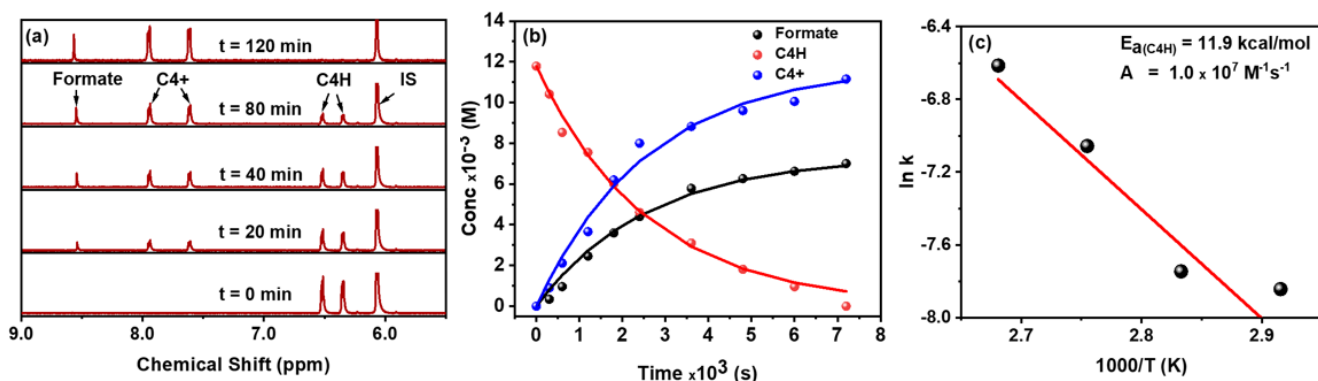
Figure 2. (a) ^{1}H-NMR spectra of a reaction mixture containing C4H and CO_2 in DMSO-d6. Reaction conditions: [C4H] = 0.01 M, [KBF$_4$] = 0.20 M, P$_{CO2}$ = ~2.2 atm, t = 100°C, and reaction times of 0, 20, 40, 80 and 120 minutes. 1,3,5-Trimethoxybenzene (0.05 M) was introduced as an internal NMR standard. (b) Scatter plot of reactant and product concentrations as a function of time for the reaction between C4H (0.1 M) and CO_2 (1.5 M). The solid lines represent the fits obtained using the kinetic model described in Section S1C, SI. (C) Plot of lnk vs 1/T for the reaction between C4H and CO_2.

formate ion (at 8.5 ppm) and the conjugate hydride acceptor C4+ (at 7.94 and 7.61 ppm) peaks were observed (Figure 2a). The increase in the C4+ concentration does not match the increase in the formate ion concentration (blue and black traces in Figure 2b), indicating that an additional HT pathway occurs (possibly reduction of DMSO, as discussed in the previous paragraph). Thus, the experimental HT data were fit to kinetic models that account for the side HT reactions (model details are available in the Section S1C, SI). The kinetic data fitting enabled the derivation of rate constants k$_{HT}$ for HT from hydride donors (R-H) to CO_2:

$$CO_2 + RH \rightarrow R^+ + HCOO^- \qquad \text{k}_{HT} \qquad (1)$$

The resulting rate constants values are in the $2 \cdot 10^{-6}$ to $2 \cdot 10^{-4}$ M^{-1} s^{-1} range (Table S2, SI). Subsequent temperature-dependent kinetic experiments were performed to determine free energy barriers ΔG‡ and the Arrhenius pre-exponential factors for HT reactions. These experiments were performed for C4H, C5H and C7H (Figures 2c and S14a and b), while other hydrides could not be measured because of the narrow temperature window in which detectable HT to CO_2 was observed. The free energy barriers for other hydride donors were thus evaluated by taking an average pre-exponential factor of $1 \cdot 10^7$ M^{-1}s^{-1} (which was obtained from C4H, C5H and C7H temperature-depended kinetic experiments). Using this pre-exponential factor, the experimental free energy barriers were found to range from 15 to 21 kcal/mol (Table S2). The experimentally determined free energy barriers are in good agreement with DFT-computed values (Table S2 and Section S2), except for C1H and C2H, where experiment yields much larger barriers than the computationally predicted values. We associate this mismatch to the poor solubility of these hydrides in DMSO, which results in aggregation and low reactivity observed in the experiment. The optimized transition state structures of R-H-CO_2 (Figure S19) demonstrate that CO_2 aligns parallel to the benzimidazole C-N bond, where the partial negative charge on O is stabilized by far-ranging interactions (<3.5 Å) with the N of the five-member ring. Faster kinetics can be correlated to several structural properties, such as shorter R-H bond lengths, longer H-CO_2 bond lengths and more linear HT (C-H-C) angles (Table S8) and all factors indicating an early transition state.

The Marcus HT formalism[34–36] was applied to the observed rate dependence on the thermodynamic driving force (ΔG^0), with the goal of evaluating the self-exchange reorganization energies associated with HT to CO_2. According to Marcus theory, the reaction barrier ΔG‡ can be expressed as:

$$\Delta G^‡ = W_r + \frac{\lambda}{4} + \frac{\Delta G^0}{2} + \frac{\Delta G^{0^2}}{4\lambda} \qquad (2)$$

Where W$_r$ is the free energy for the formation of the precursor complex (assumed here to be W$_r$=2 kcal/mol, see Section S1.C.III, SI), while the reorganization energy λ is the energy required to distort the nuclei of the product state from the initial reactant geometry to the minimum product geometry. The experimental and DFT-calculated barriers are plotted in Figure 3a, along with the fits obtained using equation (2). The fit enabled us to evaluate the reorganization energy associated with HT from R-H to CO_2 and the values of 66 and 70 kcal/mol for experimental and calculated barriers were obtained.

Before we proceed to further discuss the analysis of reaction kinetics involving CO_2, we briefly discuss the reactivity of organic hydrides toward protons. While the hydrogen-evolution reaction (HER) is often the most challenging competing process to avoid in electrocatalytic CO_2 reduction, we found that our organic hydrides reduce protons to H$_2$ in negligible yields (<2%, Section S1C.IV). These experimental results are consistent with our DFT calculated barriers for water reduction by HT form C1H-C8H, which were computed to be in the 26-32 kcal/mol range (Figures 3a and 3c and SI Section S1C.IV).

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Returning to CO_2 reduction kinetics, we further investigate different contributions to the reorganization energy λ. Specifically, λ can be expressed in terms of symmetric self-exchange reorganization energies as:

$$\lambda = \frac{\lambda_{RH} + \lambda_{CO2}}{2} \qquad (3)$$

The reorganization energies λ_{R-H} and λ_{CO2} are associated with the following self-exchange reactions:

$$RH + R^+ \rightarrow R^+ + RH \qquad \lambda_{RH}$$

$$HCOO^- + CO_2 \rightarrow CO_2 + HCOO^- \qquad \lambda_{CO2}$$
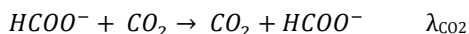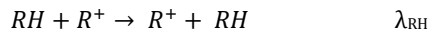
To estimate the λ_{R-H} for our organo-hydrides, the self-exchange reorganization energy for C4H was obtained experimentally to be λ_{R-H} = 91.2 kcal/mol (SI Section S1 C III(a)). This value is in excellent agreement with previously reported self-exchange energies of organic hydrides.[36] Finally, λ and λ_{R-H} values were used to derive λ_{CO2} and the value of 41 kcal/mol was obtained, which is in good agreement with the DFT calculated value (λ_{CO2} =56.4 kcal/mol, see Section S2.C, SI).
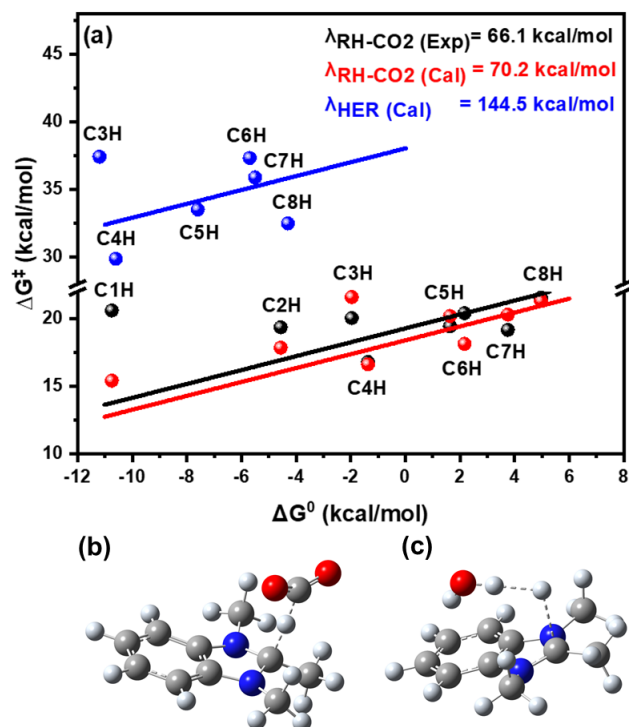
Figure 3. (a) The correlation between free energy barriers ($\Delta G^\ddagger$) and reaction free energies (ΔG^0) for HT between C1H-C8H and CO_2: experiment (black), calculation (red). Blue data show calculated values for HT to water (HER). Solid lines represent the fit to the Marcus model. (b) and (c) Calculated TS structures for HT from C4H to (b) CO_2 and (c) H_2O.

What information can be derived from these reorganization energies? To address this question, we evaluate the rate of HT for a hypothetical electrocatalyst operating at room temperature and at the thermodynamic driving force of -0.1 eV (to ensure a small overpotential). If the catalyst was made from our organic hydrides, the HT rate would be $1.7 \cdot 10^{-6}$ $M^{-1}s^{-1}$ (Table 1), which is prohibitively slow. The only way to reduce the barrier would involve identifying hydride donors with lower self-exchange reorganization energies. Indeed, metal-based hydride donors tend to have lower self-exchange reorganization energies. For example, a Ru-based hydride [Ru(trpy)(bpy)H]$^+$ was reported to have λ_{R-H}=60.0 kcal/mol,[37] which lowers our rate constant estimate to $1.1 \cdot 10^{-3}$ $M^{-1}s^{-1}$ (Table 1), a value that is still quite low. Interestingly, even if an ideal hydride donor was identified, with λ_{R-H}=0 kcal/mol, the rate constant would be relatively small ($4.5 \cdot 10^2$ $M^{-1}s^{-1}$, Table 1). This rate constant is barely sufficient for processes involving the use of solar energy, where catalytic rates in excess of 100 turnovers are needed to efficiently keep up with the photon flux at solar irradiance levels. [38,39] Also, tate constants listed in Table 1 provide a plausible explanation for the fact that electrocatalytic CO_2 reduction to the formate ion is rarely observed experimentally.

Table 1: Summary of calculated λ and hydride transfer rate constants at 25^0 C with -0.1 eV thermodynamic driving force.

Hydride Donor	$\lambda_{(R-H)}$ (kcal/mol)	$\lambda_{(H-CO2)}$ (kcal/mol)	k $M^{-1}s^{-1}$
NADH analog	91.2	66.1	$1.7 \cdot 10^{-6}$
[Ru(trpy)(bpy)H]$^+$	60.0	50.5	$1.1 \cdot 10^{-3}$
Ideal	0	20.5	$4.5 \cdot 10^2$

What can be done to circumvent the observed kinetic barriers for direct HT to CO_2? An interesting approach has been recently proposed by Yang, namely the orthogonal HT mechanism that involves a separate transfer of electrons and a proton to CO_2.[40] In this bioinspired approach, the hydride-donating catalyst is replaced by a two-component catalytic system consisting of separate electron and proton donating groups. Using thermodynamic arguments, the authors show that the orthogonal HT can be efficiently utilized to break the scaling relationships associated with conventional HT. Here, we argue that the orthogonal HT could also provide an excellent solution to the kinetic challenges associated with conventional HT, since the kinetic barriers associated with electron and proton transfers are often much lower than those for HTs.

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