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Electrocatalytic Reduction of C–C π -Bonds via a Cobaltocene-Derived Concerted Proton–Electron Transfer Mediator: Fumarate Hydrogenation as a Model Study

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ABSTRACT: Reductive concerted proton-electron transfer (CPET) is poorly developed for the reduction of C-C π -bonds, including for activated alkenes that can succumb to deleterious pathways (e.g., a competing hydrogen evolution reaction or oligomerization) in a standard electrochemical reduction. We demonstrate herein that selective hydrogenation of the C-C π -bond of fumarate esters can be achieved via electrocatalytic CPET (eCPET) using a CPET mediator comprising cobaltocene with a tethered Brønsted base. High selectivity for electrocatalytic hydrogenation is observed only when the mediator is present. Mechanistic analysis sheds light on two distinct kinetic regimes based on the substrate concentration: low fumarate concentrations operate via rate-limiting CPET followed by an electron-transfer/proton-transfer (ET/PT) step, whereas high concentrations operate via CPET followed by a rate-limiting ET/PT step.

oncerted proton-electron transfer (CPET) steps are • advantageous in catalyst design schemes as a strategy to enhance reaction kinetics.¹ Reductive CPET strategies are of interest toward the reduction of unsaturated substrates,² for example with respect to carbonyl functionalities.³ Reductive CPET with C-C π -bonds, however, remains an opportunity for chemical synthesis but is underexplored, an inherent obstacle being the large structural reorganization (sp²-to-sp³ hybridization) associated with CPET to the carbon atom of a C-C π -bond.⁴ Nevertheless, representative reports include mechanistic investigations of SmI2·H2O used in the reduction of anthracene or enamines, as reported by the Flowers and Mayer groups, respectively (Scheme 1A).^{5,6} Relatedly, studies of metal-hydride (M-H)-mediated hydrogen atom transfer (HAT/MHAT) have pointed to CPET from M-H intermediates to C-C π -bonds,^{7,8} a strategy that can be rendered catalytic when stoichiometric silane or H₂ regenerates the active catalyst.^{9–12}

Electrocatalytic CPET (eCPET) (Scheme 1B) may offer an attractive complementary approach toward C–C π -bond reductions, especially if competitive hydrogen evolution reaction (HER) and/or substrate polymerization pathways, both of which may be problematic in canonical electrode-mediated reductions,¹³ can be mitigated. Toward this end, our group has begun exploring molecular mediators that can transfer a stored H-atom equivalent, derived from an acid in solution and an electrode, to unsaturated substrates.¹⁴ Accordingly, we modified a cobaltocenium redox mediator with *N*,*N*-dimethylaniline as a Brønsted base ([CpCoCp^{NMe₂}]-[OTf]) in order to decouple the redox and protonation sites to minimize undesired HER^{15,16} while allowing for electror-reductive cycling of the mediator.

Reduction from Co^{III} to Co^{II} in this system induces bond weakening of the protonated dimethylaniline to furnish a

Scheme 1. Representative Reagents in Chemical CPET with C–C π -Bonds and Our Strategy to Extend eCPET to C–C π -Bond Reduction



homolytically weak N–H bond (N–H bond dissociation free energy (BDFE_{N–H}) = 39 kcal·mol⁻¹; Figure 1). This state of the mediator is highly reactive and was shown to reduce acetophenone via a net H-atom (H·) (Scheme 1B), with

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Figure 1. Thermochemical square scheme for CPET reduction of diphenyl fumarate, including PT (blue) and ET (red) pathways. Experimental and calculated values in MeCN are reported.

associated mechanistic data confirming a CPET process. With acetophenone, the overall reaction is selective for C–C (pinacol-type) coupling of the ketyl radical; further reduction to the alcohol (i.e., Ph(Me)CH(OH)) is not observed. To probe whether a net $2H^+/2e^-$ (2H·) transfer can instead be catalyzed by this Co-derived mediator, here we focus on C–C π -bonded fumarate esters as suitable candidates, noting their associated challenges (e.g., oligomerization and competitive HER) in traditional electrode-mediated reductions.^{17,18}

The BDFE_{C-H} for the succinyl radical derived from diphenyl fumarate (DPF) was calculated to be 48 kcal·mol⁻¹ via DFT using MeCN as the solvent, providing a substantial driving force ($\Delta G^{\circ} = -9$ kcal·mol⁻¹) with respect to a CPET step from the protonated Co(II) state of the mediator. DPF reduction should preferably occur via CPET using the [CpCoCp^{NMe₂}][OTf] mediator, as supported by thermodynamic considerations compared with initial proton transfer (PT) (ΔpK_a (MeCN, calc) = 25; $\Delta G^{\circ} = 33$ kcal·mol⁻¹) or electron transfer (ET) ($\Delta E_{1/2} = 0.5$ V; $\Delta G^{\circ} = 12.5$ kcal·mol⁻¹) (Figure 1).

Cyclic voltammetry (CV) at 100 mV/s with 1 mM $[CpCoCp^{NMe_2}][OTf]$ in the presence of 50 mM $[^{4-CN}PhNH_3]$ -[OTf] and 50 mM diphenyl fumarate at a boron-doped diamond (BDD) working electrode resulted in an electrocatalytic wave at -1.21 V vs Fc+/0. Gratifyingly, controlledpotential coulometry (CPC) with TsOH in an undivided cell at -1.30 V vs Fc^{+/0} furnished diphenyl succinate in 86% isolated yield after 20 h (Figure 2). The reaction is efficient in acid because of dramatic HER attenuation. In the absence of $[CpCoCp^{NMe_2}][OTf]\text{, the desired product was detected in just}$ 24% yield with only 26% of the starting material remaining. Using 1 mM Cp₂Co in place of [CpCoCp^{NMe₂}][OTf] gave the product in just 9% yield with only 32% of the starting material remaining (and substantial HER). Dicyclohexyl fumarate delivered a 78% yield with 2 mM [CpCoCp^{NMe2}][OTf] but only a 2% yield of the product without the mediator. Collectively, these data underscore the utility of the catalytic mediator compared with low-yielding electrode-mediated reductions;¹⁹ undesired reactivity is attenuated, and the electrocatalytic reduction occurs at lower overpotentials.

Following the analytical methods of Savéant and co-workers, k_{obs} in eq 1 reflects the rate of kinetically limiting steps in a $2H^+/2e^-$ process.^{20,21} Curiously, variation of [DPF] reveals two kinetic regimes, indicative of the interplay between two rate-determining steps (rds) (Figure 3A). At low [DPF] (5–30 mM), log(k_{obs}) increases linearly with log([DPF]) with a slope of ~1, revealing the reaction to be first-order with respect to [DPF]. However, at higher [DPF] (40–80 mM), this dependence begins to plateau toward zeroth-order, suggesting



Figure 2. (A) Cyclic voltammograms of reaction components using diphenyl fumarate as the substrate at 100 mV/s. (B) Optimized controlled-potential coulometry (CPC) conditions for eCPET reduction of diphenyl fumarate and dicyclohexyl fumarate.

that at high concentration a rate term dominates that is not dependent on [DPF].

$$i_{\rm pl} = 2FSC_{\rm cat}^0 \sqrt{D_{\rm cat}} \sqrt{k_{\rm obs}}$$
(1)

In the low-[DPF] regime, the reaction is first-order in [Co], as evidenced by a linear relationship observed between i_{cat} and [Co] with a k_{obs} value that remains constant (see the Supporting Information (SI)). We further observe an approximately zeroth-order dependence on [H⁺] (slope \approx 0.1); these observations intimate a kinetically dominant rate-limiting step involving CPET from the mediator [CpCoCp^{NHMe₂}]⁺ to DPF at low [DPF]. A second-order rate constant k_{CPET} of 14.20 M⁻¹ s⁻¹ was obtained in this regime, with $k_{obs} = k_{CPET}$ [DPF].

By contrast, at higher [DPF], where the dependence of the rate on the substrate concentration begins to plateau, a stronger dependence on $[H^+]$ is observed, with an approximate initial slope of 0.4 in the linear fit between $log(k_{obs})$ and $log([H^+])$; an eventual decrease in slope is noted at the highest $[H^+]$ studied. These observations suggest a larger kinetic influence of an acid-dependent step in the regime where $[DPF] \ge [H^+]^{.22}$

An observed shift in the kinetic dependence on the relative [DPF] and [H⁺] is also evident from an examination of the kinetic isotope effect (KIE) using [^{4-CN}PhND₃][OTf] at both high and low [DPF] concentrations (Figure 3B). In the low-[DPF] regime (20 mM), a large KIE of 4.1 ± 0.6 is observed that is similar to our previously reported KIE for O–H bond formation using acetophenone substrate via eCPET (4.9 ± 0.7).¹⁴ Alternatively, a much smaller KIE of 1.3 ± 0.1 is observed at high [DPF], providing further support that a



Figure 3. (A) Analyses of the dependence of the rate on (left) the substrate (DPF) concentration and (right) the acid ($[^{4-CN}PhNH_3]$ -[OTf]) concentration in two substrate concentration regimes. Linear fits correspond to highlighted points. (B) Kinetic isotope effect studies using $[^{4-CN}PhND_3]$ [OTf] at (left) 20 mM and (right) 50 mM DPF. (C) Hammett analysis and rate-driving force relationship with various para-substituted diaryl fumarates at a substrate concentration of 50 mM.

change in the relative rate contributions of distinct steps is operative in this system. $^{23}\,$

To account for the onset of an acid dependence at higher [DPF], we have considered several scenarios. One could involve a kinetically limiting change from an initial CPET step between $[CpCoCp^{NHMe_2}]^+$ and DPF to a multisite proton-coupled electron transfer (MS-PCET)^{24–26} involving net HAT, with the mediator as an electron source and exogenous acid as the proton source. We disfavor this scenario since a first-order dependence on *both* [DPF] and [H⁺] would be expected. Additionally, CPET from the mediator should kinetically outcompete a proton-dependent MS-PCET at high [DPF] because of the expected higher k_{obs} , which is inconsistent with the plateau behavior observed in Figure 3. We instead posit that a second elementary step, involving acid instead of DPF, becomes kinetically relevant as [DPF] increases.

$$(k_{\rm obs})^{1/2} = \frac{1}{\frac{1}{\sqrt{k_{\rm CPET}C_{\rm substrate}^0} + \frac{1}{\sqrt{k_{\rm PT}C_{\rm H^+}^0}}}$$
(2)

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An ECEC mechanism (Figure 4A), whose k_{obs} is provided by the rate law in eq 2, accommodates the collective data.





Figure 4. (A) Plausible mechanism via a catalytic ECEC pathway with a DFT-derived structure showing intermolecular association of succinyl anion with $[CpCoCp^{NMe_2}]^+$. (B) EC pathway following initial catalytic CPET.

Following initial CPET to DPF and subsequent reduction of the resulting radical (presumably faster than protonation of the generated Co(III) species), an intermediate involving the Co(III) mediator and the succinyl anion is formed; the latter is then protonated ($k_{\rm PT}$) to release the product and regenerate the CPET mediator via protonation/reduction. The catalytic current and the value of $k_{\rm obs}$ are determined by both the rate of CPET ($k_{\rm CPET}$) and the rate of protonation ($k_{\rm PT}$), thus accounting for the observed kinetic behavior. At low [DPF], $k_{\rm CPET}$ [DPF] $\ll k_{\rm PT}$ [H⁺]. Therefore, a first-order dependence on [DPF] and a zeroth-order dependence on [H⁺] is observed. For $k_{\rm CPET}$ [DPF] $> k_{\rm PT}$ [H⁺], which occurs at higher [DPF], a positive order in [H⁺] arises as the [DPF] dependence is diminished.

Rate-determining protonation of the Co(III) mediator would also account for the acid dependence observed.

However, on the basis of measurements of the rate of protonation of $[CpCoCp^{NMe_2}]^+$ (2.7 × 10⁷ M⁻¹ s⁻¹) using different acid concentrations, following Dempsey and coworkers,^{27,28} we disfavor this scenario. Such a high rate compared with k_{obs} is inconsistent with protonation of the CPET mediator being rate-limiting. This observation also disfavors a second CPET from the mediator to furnish the product, as such a pathway should not show a dependence on the acid concentration (see the SI). A catalytic EC pathway (Figure 4B), akin to that proposed previously for acetophenone,¹⁴ is also unlikely because one would expect a zerothorder dependence on the acid and/or detectable hydrodimerization products via radical homocoupling or radical/ anion addition (Figure 4A),^{17,18} inconsistent with the available data. Reduction of the succinyl radical at the electrode is sufficiently facile ($E_{calc} = -0.78$ V vs Fc^{+/0}) at the working potential of -1.30 V vs Fc^{+/0} that subsequent protonation would not be expected to influence the rate of electrocatalysis.

The shift in relative rate contributions to the overall catalysis between initial CPET and the downstream protonation step is evident at high [DPF], where the positive [H⁺] dependence decreases at the highest [H⁺] concentrations examined because of enhancement of $k_{\rm PT}$ [H⁺] relative to $k_{\rm CPET}$ [DPF] (i.e., $k_{\rm PT}$ [H⁺] $\gg k_{\rm CPET}$ [DPF]). Accordingly, reevaluation of the DPF substrate order at a very high acid concentration (150 mM), where the downstream protonation step is not predicted to be rate-limiting, displays a first-order dependence on the substrate throughout the entire [DPF] range examined (Figure 3A).²⁹

The collective kinetic data and facile reduction of the succinyl radical at our working potential suggest an interaction between the succinyl anion and Co(III) mediator. A DFT calculation (see the SI for details) supports the exergonic formation of such an intermediate ($\Delta G_{assoc} = -4.4 \text{ kcal·mol}^{-1}$), where intermolecular $\pi - \pi$ stacking can be identified (Figure 4A). Additionally, an electrostatic attraction may contribute to such an associated intermediate considering the relatively low polarity of the medium.^{30,31} As inferred from the optimized structure, protonation of the succinyl anion, with a concomitant change from C(sp²) to C(sp³) hybridization, is sterically hindered by the interaction with the Co(III) mediator, providing a barrier for this step.

Hammett analysis of 4-CF3-, 4-Cl-, 4-H-, and 4-OMesubstituted diaryl fumarates (50 mM)³² with 1 mM [CpCoCp^{NMe₂}][OTf] and 50 mM [^{4-CN}PhNH₃][OTf] (see Figure 3C) shows a clear trend in reaction rate with increasing driving force, contrasting with our previous data for aryl ketones¹⁴ but consistent with other examples of reductive CPET transformations.³³⁻³⁶ The obtained slope value of 0.83 (the Brønsted α value) is higher than the theoretical slope predicted by Marcus theory for the low driving force regime (0.5), suggesting a late transition state along the reaction coordinate. According to this relationship (Figure 3C, right, linear fit), a thermoneutral CPET to a C-C π -bond should occur with $k_{obs} = 1.5 \times 10^{-4} \text{ s}^{-1}$. This is approximately 3 orders of magnitude lower than the calculated k_{obs} of a thermoneutral CPET to the C–O π bond in acetophenone,¹⁴ supporting the notion of significantly slower CPET to a C–C π -bond because of substantial reorganization at carbon.³

In summary, using a synthetically integrated CPET mediator comprising a cobaltocenium redox center and *N*,*N*-dimethylaniline Brønsted base along with fumarate esters as model substrates, we have demonstrated reductive eCPET to achieve net hydrogenation $(2e^{-}/2H^{+})$ at -1.30 V vs Fc^{+/0}. This reactivity profile contrasts with the previously reported reactivity of ketones with this mediator $(1e^{-}/1H^{+}$ followed by C–C coupling) and demonstrates that cobaltocene can be repurposed from a competent HER (electro)catalyst to a net hydrogenation (electro)catalyst via tethering of a Brønsted base.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c03335.

Synthesis and characterization of compounds, electrochemical data and procedures, thermochemical considerations, details of DFT calculations, and Cartesian coordinates (PDF)

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Notes

The authors declare no competing financial interest.

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