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A Predictive Model for the Decarboxylation of Silver Benzoate Complexes Relevant to Decarboxylative Coupling Reactions

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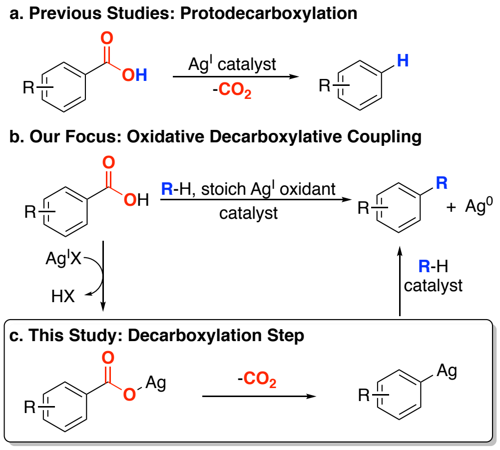
Supporting Information Placeholder

ABSTRACT: Decarboxylative coupling reactions offer an attractive route to generate functionalized arenes from simple and readily available carboxylic acid coupling partners, yet they are underutilized due to limitations in the scope of carboxylic acid coupling partner. Here we report that the field effect parameter *(F)* has a substantial influence on the rate of decarboxylation of well-defined silver benzoate complexes. This finding provides the opportunity to surpass current substrate limitations associated with decarboxylation and to enable widespread utilization of decarboxylative coupling reactions.

Oxidative decarboxylative coupling (ODC) reactions have received significant attention as benign routes to access functionalized arenes from widely available and inexpensive carboxylic acid coupling partners.[1] Despite their potential to offer efficient alternatives to traditional cross-coupling reactions, these reactions have not seen widespread utilization due, in part, to the substrate limitations commonly observed. In many ODC reactions, only *ortho*-nitro or *ortho*-fluorobenzoic acids undergo efficient decarboxylative coupling.[2-3] It is unclear if this limitation arises from the decarboxylation step and/or the coupling step(s).

In many ODC reactions Pd,[4] Cu,[2b-d] or Ni[3] catalysts are paired with Ag-based stoichiometric oxidants (Scheme 1b). Silver salts are well-known to promote decarboxylation reactions[5] and are likely responsible for the decarboxylation step in many of these catalytic coupling reactions. The influence of benzoate substitution on the decarboxylation of silver carboxylate species has been studied computationally by Su and Lin who concluded that the *ortho*-nitro group facilitates decarboxylation through the combination of a destabilizing steric effect on the starting material ground state and a stabilizing influence on the transition state from coordination of the nitro group to silver.[5b] Subsequently, Larrossa, Campanera and coworkers measured the rates of the silver-catalyzed protodecarboxylation (Scheme 1a) and found that the strong activating influence of *ortho*-nitro substituents could instead be explained by a combination of electronic and steric effects described using the Fujita-Nishioka linear free energy correlation.[6] The ability to extend these findings to decarboxylative coupling reactions (Scheme 1b) would enable both an improved understanding of the substituent trends and limitations in ODC reactions that may arise from the decarboxylation step and also the prediction of new efficient coupling partners. It has been shown in related systems that the trends observed for catalytic protodecarboxylation reactions are not the same as those observed for the decarboxylation step when measured from well-defined carboxylate complexes because the rates of complex formation and protodemetallation contribute to the overall catalytic rate.[7] Thus, the decarboxylation step is important for understanding catalytic ODC reactions, yet there are no studies that probe the decarboxylation step of

Scheme 1. (a) Catalytic protodecarboxylation and (b) oxidative decarboxylative coupling reactions.



well-defined silver carboxylate complexes. We report here a new understanding of the current scope limitations of decarboxylation gained from the synthesis and reactivity of a series of differently substituted silver carboxylate complexes (Scheme 1c).

We recently reported the synthesis and characterization of (phen)Ag(2-NO_2-benzoate) from Ag_2O and 2-nitrobenzoic acid (phen = 1,10-phenanthroline).[8] This complex readily undergoes decarboxylation at 110 °C in DMF to yield nitrobenzene and 2,2'-dinitrobiphenyl. To ensure reproducible rates and product distributions, all reactions in this study were conducted with 0.7 mM H_2O in DMF-d_7 under a N_2 atmosphere in a J. Young NMR tube.[9] Under these conditions nitrobenzene is formed as the sole product (Figure 1a). The decarboxylation of a 3.5 mM solution of (phen)Ag(2-NO_2-benzoate) at 110 °C in DMF-d_7 with 0.7 mM H_2O, follows an exponential decay and the reaction reaches 83% completion in 3 h (Figure 1b). The initial rate of decarboxylation (3.6 mM h^{-1}) was determined by fitting the early reaction times (Figure S3F). Varying the concentration of (phen)Ag(2-NO_2-benzoate) reveals a first order dependence (Figures S2 and S3). Similarly, the unligated Ag(2-NO_2-benzoate) complex undergoes facile decarboxylation when heated at 110 °C in DMF-d_7, with a reaction rate and reaction profile similar to that of (phen)Ag(2-NO_2-benzoate) (Figure S4). Thus, it appears that the phen ligand provides a minor accelerating effect in the decarboxylation of these silver carboxylate complexes.[5d] The complexes bearing phen were used for further study due to the improved isolability of a large series of complexes bearing differing benzoate substitution.

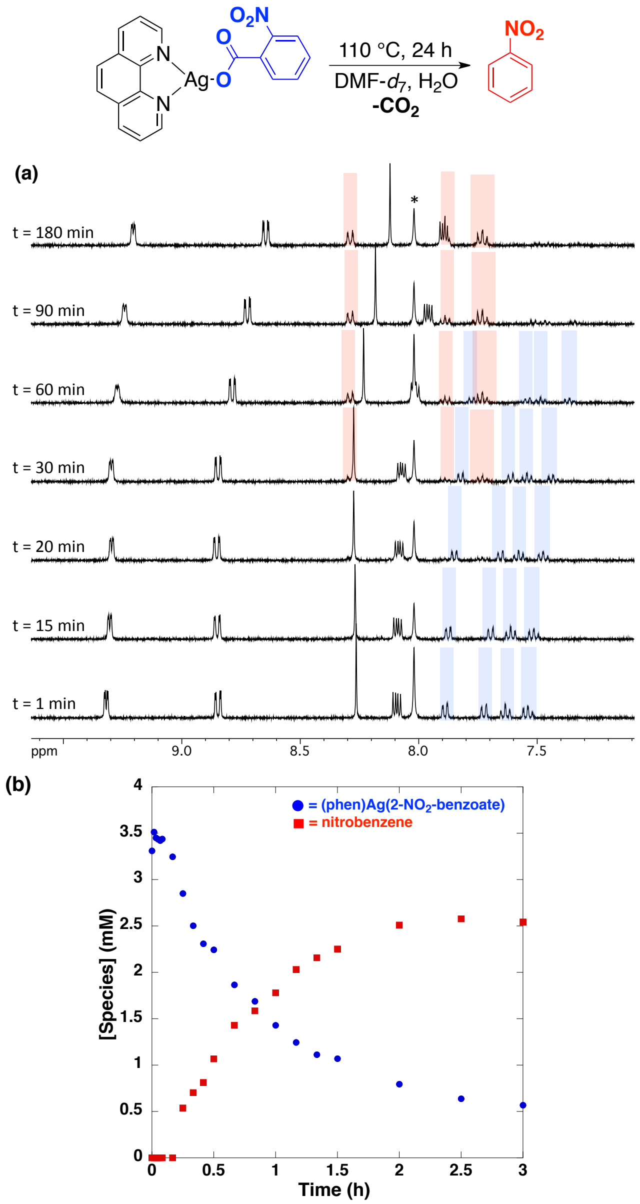


Figure 1. (a) ^{1}H NMR time course and (b) reaction profile for the decarboxylation of (phen)Ag(2-NO_2-benzoate) (3.5 mM, •) to form nitrobenzene (■) in DMF-d_7 with 0.7 mM H_2O at 110 °C. The asterisk denotes the residual solvent signals.

Under the standard decarboxylation conditions, the expected silver aryl intermediate could not be detected, suggesting that protodemetallation is much more rapid than decarboxylation in these systems. To confirm this conclusion, the corresponding silver aryl complex, Ag(2-NO_2-phenyl),[8] was synthesized independently and the rate of protodemetallation was measured both in the presence and absence of phen (Figures S5 and S6). In the presence of 1 equiv of phenanthroline in DMF-d_7 at 110 °C, Ag(2-NO_2-phenyl) undergoes protodemetallation at a rate of (15.85 mM h^{-1} at 5.4 mM).[10] The rapid rate of protodemetallation is consistent with the absence of an observable silver aryl intermediate in these decarboxylation reactions and with the calculated energy barriers previously reported for related catalytic protodecarboxylation reactions.[5d-e]

Because decarboxylation and in particular decarboxylative coupling reactions are often limited to the reactions of *ortho*-substituted carboxylates, we were interested in probing the dependence of the decarboxylation rate on the substitution of the benzoate. A series of silver benzoate complexes bearing different *ortho*-substituents, (phen)Ag(2-R-benzoate), were synthesized. Upon heating each of these complexes under the standard reaction conditions in DMF-d_7 at 110 °C, we observed much faster rates of decarboxylation for benzoates bearing inductively electron-withdrawing substituents than electron-donating ones (Figure 2a). Similar to studies of protodecarboxylation reactions,[6a] these data are well fit by the Fujita-Nishioka linear free energy correlation (Eq 1, Figure 2b),[6b,9] yet this system reveals a striking dependence on the Swain-Lupton-Hansch field effect parameter (8.428F), while the Hammett (-1.392σ) and steric (0.204E$_s$) coefficients are small.

$$\ln(k_R/k_{Me}) = a\sigma + bEs + cF + d \quad (1)$$

The influence of the field effect parameter (F) decreases with distance from the reaction site and thus the field effect is negligible for *meta*- and *para*-substituted benzoates.[6b,11] To further probe the importance of the field effect, the *meta*-nitro- and *para*-trifluoromethylbenzoate silver complexes were synthesized and heated under the standard reaction conditions. In each case the rate of decarboxylation is slow (0.066 mM h^{-1} and 0.108 mM h^{-1} respectively) reaching less than 10% conversion after 2 h (Figures S12 and S13). These data are consistent with the field effect parameter of the *ortho*-substituents being the dominant factor influencing the rate of decarboxylation. To explore the generality of this trend, the inclusion of a large array of mono- and di-substituted carboxylates were studied. This large series of carboxylates provides further refinement of the correlation. While the coefficients for the minor contributors σ and E$_s$ undergo a small change, the field effect parameter remains large and continues to dominate the correlation (7.210F, -0.022σ, 0.272E$_s$, Figure 3a). These data confirm the influence of the field effect in enhancing the rate of decarboxylation. Although the Fujita-Nishioka correlation has been applied to a number of organic transformations,[12] we are unaware of any examples in which the field effect coefficient is orders of magnitude larger than the steric or Hammett coefficients. This strong dependence on the field effect suggests that decarboxylation of these complexes proceeds by a polar transition state that is stabilized by the electrostatic effects of the nearby *ortho*-substituent.[13]

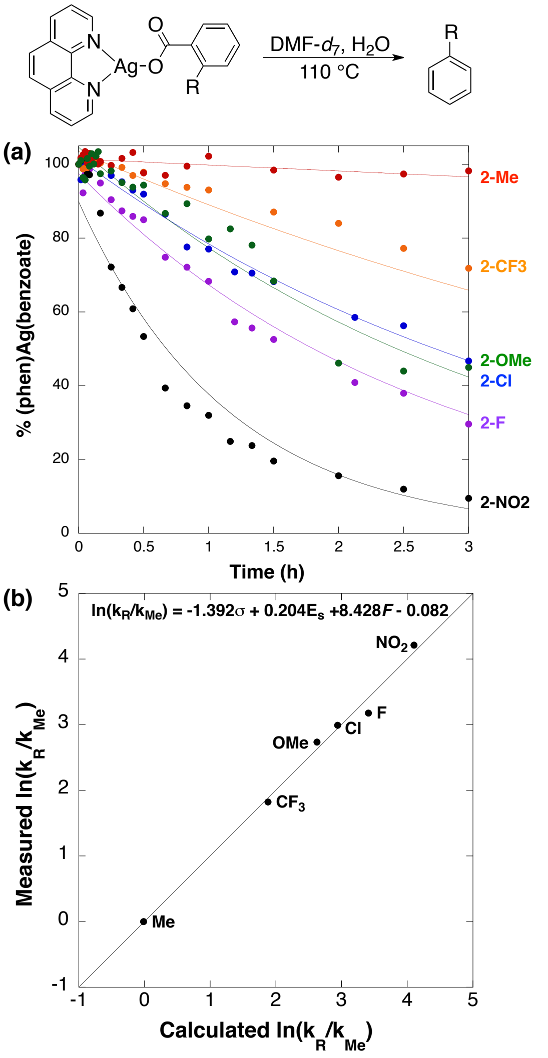


Figure 2. (a) Kinetic profiles for the decarboxylation of (phen)Ag(2-R-benzoate) where R is: Me, CF_3, OMe, Cl, F, and NO_2. Traces are included to guide the eye and are not fits. Standard reaction conditions: 8 mM (phen)Ag(2-R-benzoate), 0.5 mL DMF-d_7 with 0.7 mM H_2O at 110 °C. (b) Fujita-Nishioka Linear free energy correlation fit to the rates of decarboxylation of (phen)Ag(2-R-benzoate) in DMF-d_7 at 110 °C. Time course data and initial rate fits are included in the Supporting Information (Figures S3C and S8-12).

Because of the strong dependence on the field effect parameter (F) observed in this system we explored the possibility of correlating the rates directly with F. A plot of log(k) versus F shows a strong correlation and enables the rapid prediction of carboxylates that undergo efficient decarboxylation. To illustrate the predictive power enabled by these findings we synthesized several additional silver carboxylate complexes and measured their rates of decarboxylation (Figures S27-S31). Gratifyingly, the measured rates of decarboxylation of these benzoate complexes are well-predicted by the field effect parameter (Figure 3b, red squares). For example, the rates of decarboxylation of the 2-Me-6-NO_2-benzoate (k = 0.56 h^{-1}, F = 0.65) and the 2-Cl-6-NO_2-benzoate (k = 3.45 h^{-1}, F = 1.07) complexes show reasonable fits to the correlation. Furthermore, the 2-tosylbenzoate complex (F = 0.53) undergoes facile decarboxylation (k = 0.203 h^{-1}). This result is notable because this is a synthetically attractive carboxylate that is easily accessible from salicylic acid and can be further functionalized or deprotected.[13]

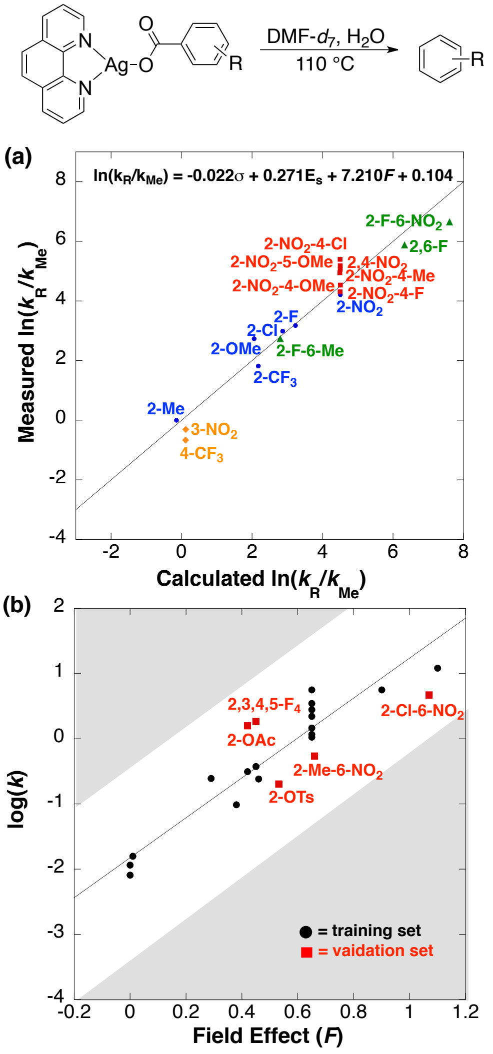
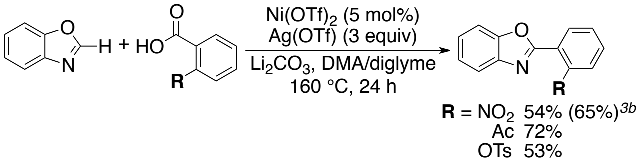


Figure 3. (a) Fujita-Nishioka Linear free energy correlation fit to the rates of decarboxylation of (phen)Ag(benzoate) complexes in 0.5 mL DMF-d_7 with 0.7 mM H_2O at 110 °C. Time course data and initial rate fits are included in the Supporting Information (Figure S11-S26). (b) Correlation of the log(k) with the field effect parameter (F). The gray area indicates the approximated experimental error in log(k).

The rapid decarboxylation of benzoates bearing substituents with large field effect parameters is consistent with literature reports in which the ortho-NO_2- (F = 0.65) and pentafluoro-substituted (F = 0.90) benzoates are efficient coupling partners in ODC reactions.[2-4] Thus, we wondered whether a high field effect value may not only facilitate decarboxylation, but also decarboxylative coupling. The nickel-catalyzed decarboxylative arylation reported by Kalyani and coworkers[3b] is an attractive test reaction because it utilizes bench-stable reagents and employs Ag(OTf) as the oxidant, yet this reaction appears to be limited to *ortho*-nitro and fluorobenzoates (Scheme 2). We sought to employ this reaction to probe the possibility of using our findings to expand the scope of decarboxylative coupling reactions. Utilizing the *ortho*-tosylate- (F = 0.53) and *ortho*-acetyl- (F = 0.33) substituted carboxylates under the reported reaction conditions results in formation of the corresponding coupling products in yields (53% and 72% respectively) that are similar to those obtained with the *ortho*-nitrobenzoic acid (54%). This result highlights the ability to utilize synthetically attractive carboxylates in previously limited ODC reactions.

Scheme 2. Ni-Catalyzed Decarboxylative Arylation[3b]



In conclusion, we have evaluated the role of benzoate substitution on the rate of decarboxylation of well-defined silver benzoate complexes. The rate of decarboxylation is influenced predominantly by the field effect parameter, enabling prediction of benzoates that undergo facile decarboxylation. We have demonstrated this predictive power by measuring the rates of decarboxylation of several new benzoates including the *ortho*-tosyl-, tetrafluoro-, and 2-Cl-6-NO_2-substituted benzoates and highlighted the synthetic power of this finding with the efficient catalytic decarboxylative coupling of the *ortho*-tosyl- and *ortho*-acetyl-substituted carboxylates. We anticipate that this work will further enable the widespread utilization of decarboxylation and decarboxylative coupling reactions.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, kinetic data, spectral data, ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(10) In the absence of phen, the rate of protodemetallation of Ag(2-NO$_2$-phenyl) is 25.5 mM h^{-1}. See supporting information for details.

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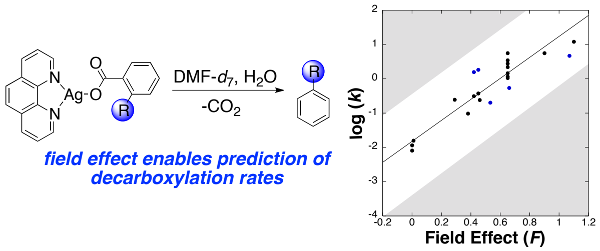

field effect enables prediction of decarboxylation rates