

There's Still Plenty to Do in Photocatalysis

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Abstract: Photocatalysis has undeniable promise for enabling chemical synthesis in a post-fossil resource future; however, this promise has yet to be realized at scale despite over 100 years of interest. Here I propose that this relatively slow progress is rooted in the high chemical complexity of photocatalytic reactions. While the complexity of light absorption and excited state chemistry is a key contributor, our research on Fe/S photocatalysis implicates the efficiency of the many thermal, dark elementary steps being the primary challenge for making a functional reaction. These experiences suggest a paradoxical opportunity in photocatalysis research: one of the richest, most enabling, and most underexplored areas of research is the study of non-photocatalytic steps.

Keywords: Kinetics · Mechanism · Photocatalysis · Radicals



Julian G. West obtained his BSc (Honours) in Chemistry at the University of British Columbia before pursuing doctoral studies at Princeton University as an NSF Graduate Research Fellow advised by Erik Sorensen. Following graduation, he was an NIH and Resnick postdoctoral fellow at Caltech with Harry Gray and Brian Stoltz before beginning as an assistant professor of chemistry at Rice University. His research

accomplishments are focused on development and mechanistic understanding of reactions catalyzed by earth abundant elements and have been recognized by numerous awards including Forbes 30 Under 30, C&EN Talented 12, and the 2025 Grammatikakis Neumann Prize.

1. Introduction

“On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is.”

So wrote Giacomo Ciamician in his 1912 Science perspective article ‘The Photochemistry of the Future’, proposing photochemical reactions as the natural solution to sustaining society after the exhaustion of nonrenewable fossil resources.^[1] While this vision of endless glass reactors covering cityscapes has not yet come to pass more than 100 years after publication, in some ways modern society increasingly resembles this picture.

Perhaps most directly, rooftops and fields are increasingly playing host to photovoltaic (PV) panels with ever-rising efficiency. By one estimate, 8.7% (2,778 TWh) of global electricity generation in 2025 was solar,^[2] with the vast majority of this generation *via* PV panels. This trend is more a triumph of photophysics than photochemistry, however, with the basic mechanics of energy transduction arising from separating photogenerated hole-

electron pair polarons at the P-N junction of semiconductors. This process allows significant storage of energy as electrical potential; however, there is no possibility of making direct chemical change. Additionally, the ability of this widespread technology to impact chemical manufacturing has an intrinsic energy efficiency limit, with the ~20%^[3] efficiency of current commercial PV panels and ~94%^[4] efficiency of electrical transmission leading to an ~81% energetic loss before the captured energy can be used to make molecules.

Direct photochemistry presents significant potential upside for efficient manufacturing of the molecules of modern life. Not only does direct photochemistry avoid the compounding energetic losses of PV generation and electrical transmission, but it also simplifies infrastructure in many ways, with relatively straightforward engineering interventions such as parabolic concentrators enabling acceptable levels of light flux for many processes under solar irradiation.^[5] Additionally, direct photochemistry has the benefit of the direct synthesis of the desired products, taking starting materials to transformed products with nothing more than incident photons of the appropriate wavelength.

Given this argument, why do we not have forests of glass tubes containing marvelous photochemical reactions to make the molecules of modern life? Why have chemists not yet delivered on this tantalizing dream?

As a chemist who has focused on the development and understanding of photocatalytic reactions,^[6–24] I propose that chemical complexity of developing photosynthetic cascades is the main reason we do not have Ciamician’s photochemical factories today. This complexity is twofold, with much effort rightly focusing on perhaps the most obvious of the challenges: the efficient absorption (and conversion to useful chemical potential) of light.^[25] Photophysical instrumentation capable of measuring ultrafast excited state dynamics are still relatively new on the timescale of 114 years,^[26] and understanding of what makes an efficient absorber and long (enough)-lived excited state capable of useful chemistry continues to be refined using these tools. Much progress has been made in the realm of noble metal photoredox catalysts such as ruthenium and iridium polypyridyl photosensitizers, where well-defined optical redox signatures are present and excited state lifetimes are quite long. This understanding has allowed for extremely efficient noble metal photoredox catalysts to be developed and rationally modified to enable certain classes of photocatalytic reactions.^[25]

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By contrast, comparable understanding of the photophysics of earth abundant photocatalysts, especially iron,^[27–29] has not yet been achieved.^[30,31] Species such as iron present significant logistical challenges for these studies, including coordinational lability, ultrashort excited state lifetimes, and the need for specialized techniques such as ultrafast X-Ray absorption and scattering^[32] to characterize the relevant electronic states. This challenge impairs the ability to rationally improve the photophysical properties of these catalysts and can lead to diminished efficiency. This lack of fundamental understanding and rational design principles has certainly been felt in my own research, where it is often not obvious how to improve the photophysical properties of iron photocatalysts. This is a limitation that I hope will be solved by increased photophysical understanding; however, it is not the most arduous step for making functional and efficient photocatalytic reactions.

In my experience, the key challenge needing to be overcome for delivering a useful photocatalytic reaction is understanding and optimizing the steps not requiring light. While the photostep of a photocatalytic reaction is absolutely necessary for reactivity by definition, it is outnumbered, often dramatically, by thermal ‘dark steps’. Still, the central nature of the photostep can lead to researchers in photocatalysis focusing on its characterization at the expense of dark processes. Knowledge of the photostep can be especially useful if it is globally limiting for the reaction; however, this is only true if the complicated choreography of dark steps is functioning efficiently.

2. My Experience in Photocatalytic Reaction Development

Here I show that understanding the thermal ‘dark side’ of photochemical reactions has been at least as important as - if not more important than - understanding the photostep in design and realization of new photocatalytic reactions in our laboratory. Asking questions in this relatively neglected part of photocatalysis has been the key time and time again for overcoming synthetic limitations and delivering some truly complex (and ideally useful) reactions.

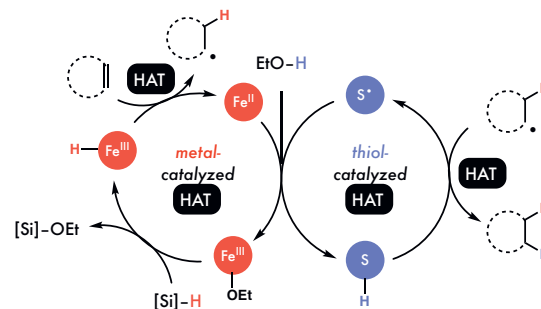
2.1 Completely Dark Reactions Can Be Illuminating for Photocatalysis

Fitting this theme, our foray into photocatalysis began with exploring a completely dark, thermal reaction: radical hydrogenation *via* successive hydrogen atom transfer (HAT) events from catalysts with different bond strengths.^[21,33–35] In this scheme, a weak (<30 kcal/mol) metal hydride could directly engage an unactivated alkene *via* HAT to form a slightly stronger (30–50 kcal/mol) C–H bond and an alkyl radical intermediate.^[36–39] This intermediate could then be engaged in HAT from a second thiol catalyst with a much stronger (80–85 kcal/mol) S–H bond to form a strong (~100 kcal/mol) C–H bond,^[40] completing the hydrogenation.^[41] While forming hydrogenated products using this cooperative HAT (cHAT) scheme was certainly of interest, one major question we had going into this study was whether these metal and thiol HAT donors could cooperate themselves and be rendered catalytic.

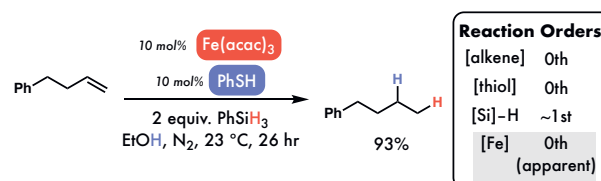
Toward potential catalysis, we envisioned that iron and thiophenol might be suitable cocatalysts (Fig. 1). Not only did the bond strengths of Fe(III)–H (~17 kcal/mol)^[36] and PhS–H (84 kcal/mol)^[41,42] meet the thermodynamic requirements for performing the cHAT hydrogenation, but they also provided a potential means of mutual turnover. We reasoned that the byproducts of these two HAT steps, Fe(II) and PhS• (or the redox equivalent PhSSPh), might interact in the presence of a proton donor to form Fe(III) and regenerated PhSH. Hydride transfer from a silane would then regenerate Fe(III)–H,^[36] preparing these species for catalysis again.

Despite the relatively undefined nature of this Fe/S interaction in our initial proposal, Kattamuri and I were delighted to

a. proposed catalytic cycle for thermal alkene hydrogenation with Fe/S via cHAT



b. kinetics data for thermal alkene hydrogenation with Fe/S cocatalysis



c. study revealed key equilibrium between Fe(III)/SR and Fe(II)/0.5RSSR

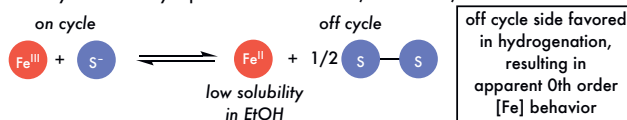


Fig. 1. Key mechanistic findings in thermal hydrogenation using Fe/S catalysis.

find this system was competent for catalysis, enabling a wide range of alkenes to be hydrogenated.^[33] We were also able to demonstrate the cooperative delivery of hydrogen atoms from orthogonal catalysts through various studies including isotope labeling experiments.

After this first demonstration, we dove into a more detailed mechanistic investigation with the Holland and Miller groups to better understand the minutiae of this catalytic system.^[35] Initial kinetic characterization by both initial rates and Variable Time Normalization Analysis (VTNA) revealed a puzzling result, namely that the reaction was positive (~1st) order in [silane] and ~0th order in all other components. We had hypothesized that Fe(III)–H generation would be the rate determining step based on previous studies of Fe(III)–H HAT reactions using silanes;^[36] however, the 0th order [Fe] dependence was inconsistent with this at first glance.

Further investigations *via* catalyst decomposition tests, Mössbauer, paramagnetic ¹H NMR, and stoichiometric studies revealed that iron speciation could explain this observation. Specifically, combining Fe(III) and PhSH in ethanol rapidly results in the formation of poorly soluble Fe(II) and PhSSPh with a small amount of Fe(III) remaining.^[35] This reaction was shown to be an equilibrium, with Fe(II) and PhSSPh able to serve as competent precatalysts for the reaction; however, in the case of hydrogenation in ethanol, it lies heavily towards the off-cycle and relatively insoluble Fe(II) and PhSSPh under catalytic conditions (Fig. 1). The dominance of this off-cycle behavior provided an explanation for the apparent 0th order [Fe] dependence, supporting Fe(III)–H formation as the rate limiting step in this chemistry.

Aside from demonstrating that thermal hydrogenation was possible using Fe/S catalysis and Fe(III)–H generation is the likely slow step for this reaction, a critical insight from these studies was identifying the equilibrium between Fe(III)/RS–H and Fe(II)/RSSR under catalysis. This equilibrium suggested a high degree of redox compatibility and flexibility between these two catalytic species, emboldening us to explore if Fe/S catalysis might be gen-

erally robust and extensible to new reactivity modes, especially photocatalysis.^[21]

2.2 Photocatalysis Mechanistic Investigation Can Appear (Misleadingly) Simple

Given the apparent efficiency of dark steps aside from Fe(III)–H formation in thermal hydrogenation using Fe/S catalysis,^[33,35] we initially wondered if replacing this step with a photostep might enable an efficient photoreaction. We immediately thought of light-induced homolysis (LIH),^[43] likely *via* ligand-to-metal charge transfer (LMCT),^[44,45] of an Fe(III) carboxylate complex to form a carboxyl radical intermediate and an Fe(II) species as a potential candidate, given the growing interest at the time in Fe(III) LMCT chemistry.^[46–49] Importantly, this post-LIH Fe(II) intermediate is analogous to that formed after Fe(III)–H HAT,^[33–36] permitting mapping onto the same catalytic framework (Fig. 2). The carboxyl radical could then rapidly decarboxylate to furnish an alkyl radical which could then be reduced by RS–H HAT, resulting in net deletion of the carboxylate, or protodecarboxylation. Finally, regeneration of the two catalytic species *via* interaction of Fe(II), RS[•], and a proton source could occur analogously to cHAT hydrogenation.^[6]

Initial reaction development by Lu and I identified several departures from the Fe/S hydrogenation system, including a biphasic 1,2-dichloroethane (DCE)/water system and the combination of Fe(III)(NO₃)₃•9H₂O and the tridentate ligand di(2-picoly)amine (DIPICA) as the preferred iron catalyst (Fig. 2).^[6] Additionally, it was found that the more sterically-demanding 2,4,6-triisopropylphenylthiol (TRIPSH) was beneficial for reactivity, presumably through discouraging occupation of Fe(III) sites needed for carboxylate coordination. Using these conditions under 390 nm

irradiation in combination with 0.1 equiv. Na₂CO₃ allowed a wide range of carboxylic acids to be deleted in high yield. In particular, acids bearing extremely electron rich aromatic rings incompatible with traditional outer-sphere oxidative photoredox catalysis^[50] functioned exceptionally well, permitting selective carboxylic acid engagement as a result of the inner-sphere LIH process.

Mechanistically, our initial kinetic investigations of a simple primary carboxylic acid substrate using the method of initial rates showed the reaction to be 0th order in all reaction components and ~1st order in [light]. This suggested a light-limited reaction and recommending increasing photon flux as the first area to improve the reaction. However, we knew from Fe/S hydrogenation that thiol RS–H HAT could become incredibly slow for certain specific substrates, particularly the reduction of benzylic radicals to form relatively weak (~88 kcal/mol) C–H bonds.^[33,34] This sluggishness can be rationalized by the Marcus-like behavior of HAT reactions, with lower thermodynamic driving forces often resulting in slower rates of HAT.^[51–53] We hypothesized that benzylic carboxylic acids might similarly result in a slow RS–H HAT, potentially slow enough to become rate determining. We performed a follow-up kinetic isotope effect (KIE) experiment using the primary acid from our kinetics study and found no KIE (~1), consistent with the observed light limited behavior. However, when a benzylic acid was used a strongly primary KIE of 3 was observed, indicating the RS–H HAT dark step becomes the rate determining step of the reaction (Fig. 2).

A key takeaway of this study is the importance of substrate molecule identity when considering kinetic behavior of a photocatalytic reaction.^[6] Indeed, if we had simply stopped analysis after obtaining light-limited behavior for a single substrate example, we could have erroneously concluded that the reaction was universally light limited and photon flux optimization would be the most important factor for process improvement and applications. However, understanding of the RS–H HAT dark step from thermal Fe/S hydrogenation studies^[33–35] led us to hypothesize this could become the rate limiting step in benzylic acid cases. KIE studies provided unequivocal evidence for this kinetic crossover, demonstrating the RS–H HAT step, and not the photochemical LIH step, to be the key target for process optimization for benzylic acids.^[6] Consistent mechanistic behavior across different substrate classes is not guaranteed in photocatalysis.

2.3 Increasing the Complexity of Dark Steps Increases the Complexity of Photocatalytic Reaction Kinetics

Given the efficiency of photocatalytic protodecarboxylation using Fe/S catalysis,^[6] we wondered if strategic modification of the dark steps might allow a new, complexity-generating synthetic reaction to be realized. Specifically, we wondered if modulating the radical polarity^[54,55] of the organic radical formed post-decarboxylation to be more electron deficient might enable addition to an unactivated alkene, opening the door to alkene hydroalkylation (Fig. 3).

In addition to the thermodynamic Marcus-like behavior,^[51–53] it is known that the rates of the HAT steps are influenced by radical polarity matching,^[56] with the fastest transfer occurring to electron-rich alkyl radicals given the electron-deficient nature of RS–H.^[54] Thus, if we engaged an electron deficient carboxylic acid, such as trifluoroacetic acid (TFA), in Fe(III) LIH decarboxylation, the slow rate of direct RS–H HAT to the [•]CF₃ radical might permit this intermediate to undergo other productive chemistry, such as rapid, polarity matched addition to an unactivated alkene.^[7] Further, the nature of this alkene addition step is such that addition should occur preferentially to the less substituted carbon, resulting in anti-Markovnikov selectivity.^[57]

This understanding of the RS–H dark step and proclivities of the electron deficient radical allowed us to propose a photocatalytic alkene hydrofluoroalkylation process using a slightly ad-

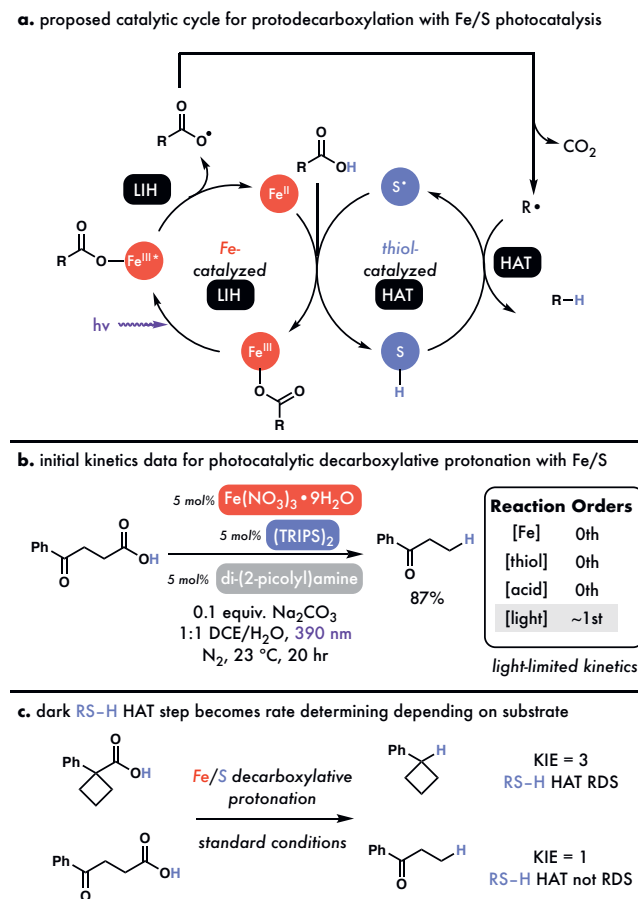
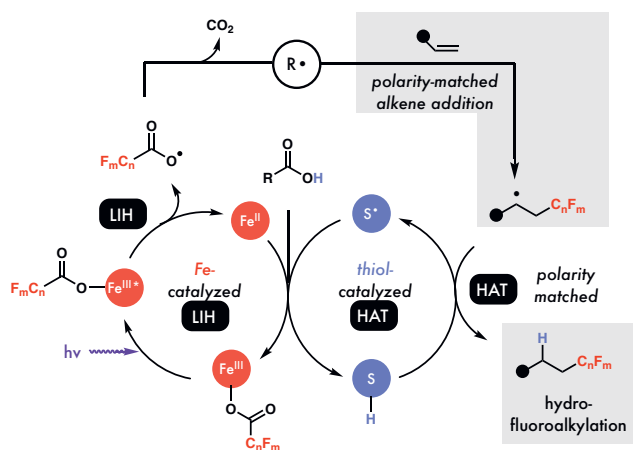
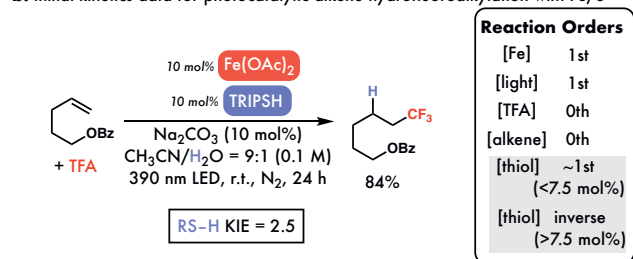


Fig. 2. Key mechanistic findings in photocatalytic protodecarboxylation using Fe/S catalysis.

a. introducing a polarity-matched alkene addition permit hydrofluoroalkylation



b. initial kinetics data for photocatalytic alkene hydrofluoroalkylation with Fe/S



c. new dark side reaction consumes thiol at higher [RS-H], impeding catalysis



Fig. 3. Key mechanistic findings in photocatalytic hydrofluoroalkylation using Fe/S catalysis.

justed Fe/S cocatalytic system.^[7] The broad catalytic mechanism framework of this reaction remains unchanged from the protodecarboxylation reaction except for the incorporation of a radical alkene addition before RS–H HAT. Experimentally, we found this reaction to function well in monophasic acetonitrile, a solvent that is known to solubilize both Fe(III) and Fe(II) species well^[58] and to have excellent transparency to near-UV light. A variety of [Fe] precursors were found to be competent for the reaction and TRIPSH and the corresponding disulfide TRIP₂S₂ were similarly found to have high reactivity similar to the protodecarboxylation. Additionally, an added ligand was not found to be beneficial for this reaction, potentially due to the competitive ligation of the solvent acetonitrile, present in large excess (Fig. 3).

Kinetic analysis of this reaction immediately presented a more complicated picture than protodecarboxylation. We initially observed 0th order behavior in [TFA] and [alkene] and 1st order behavior in [Fe] and [light], and [RS–H] (Fig. 3).^[7] This interesting collection of results was easier to interpret after performing a companion thiol RS–H HAT KIE study, where a primary (2.5) KIE was observed, suggesting rate determining character. Given that RS–H can only be regenerated by photochemically-formed Fe(II), these data painted the picture of thiol RS–H being the canonical ‘slow step’ of the reaction, dependent on upstream photochemical formation mediated by [Fe]. The 0th order behavior on [TFA] and [alkene] might be explained by saturation behavior given their excess compared to catalytic RS–H.

This result suggested that further increasing [RS–H] could be one way to accelerate the reaction; however, when the concentration was increased beyond 7.5 mol% we found the rate of the photocatalytic reaction to actually decrease, exhibiting inverse order kinetics (Fig. 3). Part of this decrease can be understood from

the Fe(III)/RS–H and Fe(II)/RSSR equilibrium characterized in studying Fe/S hydrogenation,^[35] with excess [RS–H] driving the equilibrium toward LIH-inactive Fe(II) and HAT-inactive RSSR. However, our investigation of reactions at high [RS–H] revealed another culprit: formation of an RS–CF₃ catalyst decomposition product.^[7] Indeed, at high [RS–H] concentrations, thiol-derived species are at sufficient concentration to capture [•]CF₃ and become deactivated as a thioether side product, paradoxically decreasing the [RS–H] and preventing productive [•]CF₃ addition to the alkene substrate.

Together, these studies showed that even a relatively minor addition to the dark steps of a photocatalytic cascade reaction can significantly complicate the mechanistic picture. Similar to our protodecarboxylation finding,^[6] the dark RS–H HAT step was found to have significant rate determining character.^[7] However, in this system we found upstream iron photochemistry to contribute to rate behavior, leading to 1st order dependence on [Fe] and [light] as well. Attempts to ameliorate the slow RS–H HAT step by increasing [RS–H] were stymied most notably by the emergence of a new catalyst decomposition pathway. These results underline the importance of fully understanding the dark steps available within a given photocatalytic system across possible operating conditions, including those unrelated to the desired product formation, in order to improve process efficiency.

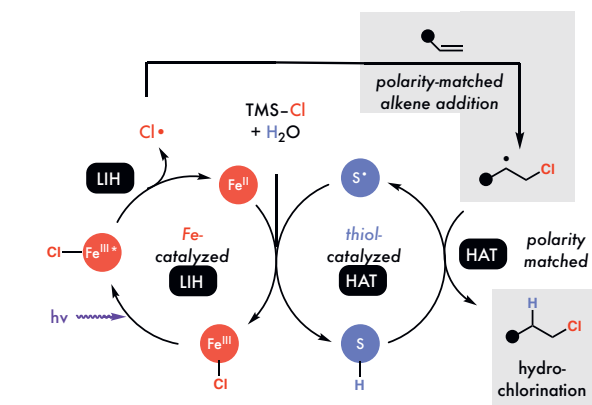
2.4 Lessons from Previous Mechanistic Studies Can Enable Cleaner Dark Reaction Kinetic Behavior

Given the observed reactivity of Fe/S photocatalysis for hydrofluoroalkylation,^[7] we considered that other alkene hydrofunctionalizations might be possible by replacing the fluorocarboxylic acids of the hydrofluoroalkylation with other nucleophilic anions.^[8,19] Previous work from our lab^[12] and others^[29,47] indicated that simple chloride anions can be similarly activated by Fe(III)–Cl LIH to form Cl[•] electrophilic radicals. These radicals can then readily add to unsaturated hydrocarbon moieties such as alkenes and alkynes.^[12,59] Given this, we hypothesized that alkene (and alkyne) hydrochlorination could be possible with anti-Markovnikov selectivity using this same Fe/S photocatalytic framework (Fig. 4).^[8]

In terms of alterations to the system, we immediately foresaw side reactivity between TRIPS–H and the sterically-unencumbered Cl[•] as a potential liability to the system, similar to that observed between TRIPS–H and [•]CF₃ in hydroalkylation.^[7] Indeed, in some ways this side reactivity was exacerbated, with use of TRIPS–H under almost identical conditions to hydrofluoroalkylation with TMSCl as the chloride source leading to low 15% formation of the desired product.^[8] To discourage this reactivity, we changed the RS–H catalyst to 4-fluorothiophenol, removing further electron density from the thiol to disfavor side reactivity with the electrophilic Cl[•]. This change alone led to nearly doubling the reaction yield, with further optimization furnishing the hydrochlorinated product in 89% yield.

Preliminary kinetic investigations revealed a similar picture to that initially found for hydrofluoroalkylation,^[7] with 0th order dependence on [Cl[•]] and [alkene] and 1st order dependence on [RS–H], [Fe], and [light] (Fig. 4).^[8] The observation of a moderate primary RS–H HAT KIE (2.1) suggested an analogous mechanistic picture, with the slow step of the reaction proposed to be RS–H HAT dependent on upstream iron photochemistry. However, the lower proclivity of 4-fluorothiophenol to interact with electrophilic radicals led us to question whether we could explore higher [RS–H] regimes without introducing catalyst decomposition side reactions such as that observed in hydrofluoroalkylation.^[7] Happily, we found this to be the case, with increasing [RS–H] up to 40 mol% maintaining 1st order behavior with respect to this species. Interestingly, at 40 mol% thiol, the reaction becomes 0th order in [Fe] and [light], further supporting the rate dependence of

a. hydrochlorination is mechanistically similar to hydrofluoroalkylation



b. initial kinetics data for photocatalytic alkene hydrochlorination with Fe/S

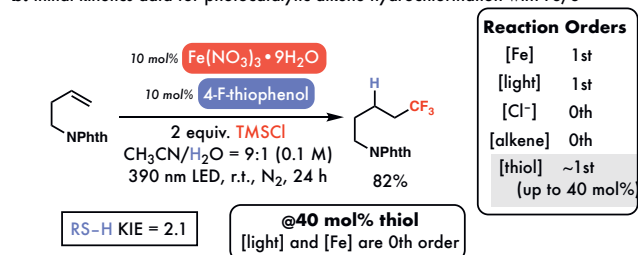


Fig. 4. Key mechanistic findings in photocatalytic hydrochloroalkylation using Fe/S catalysis.

the reaction on these species at lower [RS-H] being due to their contributions to RS-H regeneration.

Together, these studies demonstrate how mechanistic insight into dark side reactions can allow rational catalyst modification to shut down these undesired pathways in photocatalytic reactions. While the overall kinetic picture of hydrochlorination^[8] is similar to hydrofluoroalkylation,^[7] the simple change from TRIPS-H to 4-fluorothiophenol allowed for RS-H side reactivity to be mitigated and this cocatalyst to be used effectively at much higher concentrations than in hydrofluoroalkylation. Not only does this increase in dark catalyst [RS-H] permit the global reaction rate to be accelerated, but it also removes dependence on [light] and [Fe] photocatalyst under the conditions tested, allowing for cleaner kinetic behavior and simplified process optimization.

3. Conclusions

Photocatalysis presents unparalleled opportunities for manufacturing the molecules of modern life in a post-fossil resource future. However, this potential is counterbalanced by the fearsome chemical complexity of photocatalytic reactions, with the productive harmonization of myriad elementary steps presenting a serious challenge to chemists. Hidden within this challenge is another opportunity: the ability to study dark steps cooperating with photochemistry and enable rational optimization of the dark side of photocatalysis. Understanding the complexity and implications of the thermal, dark steps of cascade reactions has been critical for the application of Fe/S catalysis in challenging synthetic contexts, including protodecarboxylation, hydrofluoroalkylation, and hydrochlorination, and none of these reactions would have been possible without prior mechanistic study of a thermal Fe/S hydrogenation. Investigations of the dark steps of these photocatalytic reactions have revealed important reaction characteristics such as kinetic bifurcations based on organic substrate used, paradoxical kinetic behavior due to dark catalyst decomposition pathways at high concentrations, and multiple cases of a rate determining dark reaction kinetically depending on an upstream photoreaction. These insights have allowed rational modification of our Fe/S

catalyst system to achieve higher rates and cleaner kinetic behavior, underlining the central importance of holistic mechanistic study and physical organic chemistry to photocatalysis. I strongly believe that delving into the dark side of photocatalysis is one of the richest areas of study and fastest ways to ‘the photochemistry of the future’ and hope that these case studies provide inspiration for others to dive into this intriguing area. There is still plenty to do in photocatalysis, especially when looking away from the light.

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Author Contributions

J. G. W. conceived, wrote, and edited the manuscript.

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