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Visible-light-driven alkene dicarboxylation with formate and CO₂ under mild conditions†

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Low-cost formate salt was used as the reductant and part of the carboxyl source in a visible-light-driven dicarboxylation of diverse alkenes, including simple styrenes. The highly competing hydrocarboxylation side reaction was successfully overridden. Good yields of products were obtained under mild reaction conditions at ambient temperature and pressure of CO₂. The dual role of formate salt may stimulate the discovery of a range of new transformations under mild and friendly conditions.

Introduction

Over the past decade, great progress has been made in the catalytic utilization of carbon dioxide (CO₂) using visible light.¹ However, many of these transformations require the use of stoichiometric reductant. Recently, we developed an arylcarboxylation of alkenes with CO₂ using formate salt as a low-cost terminal reductant and also as part of the CO₂ source.² In this study, it was first realized that the CO₂ radical anion (CO₂^{•-}) ($E_{1/2}(\text{CO}_2/\text{CO}_2^{\bullet-}) = -2.2 \text{ V vs. SCE}$),³ readily available from the formate *via* hydrogen atom transfer (HAT), could be used as a potent reductive intermediate for direct reduction of substrates in visible-light-induced organic synthesis, avoiding the need to generate a highly reductive photocatalyst (PC). This discovery has been employed in a series of photocatalytic reactions involving challenging reduction of substrates recently.^{4–6} Moreover, in the control experiments of this work, we also discovered dicarboxylation and hydrocarboxylation of alkene **1a** in the absence of an aryl halide (Scheme 1a).² Afterwards, the groups of Jui,^{4a} Wickens,⁷ Li,⁸ and Mita⁹ also proved that CO₂^{•-} generated from formate could act as a source of carboxyl *via* Giese-type radical addition to alkenes and (hetero) aromatics to deliver hydrocarboxylation reactions.^{10,11} Since formate could potentially be produced from CO₂, *e.g.* *via* hydrogenation, photoreduction and electroreduction,¹² the use of formate for the dicarboxylation of alkenes to produce diacids can be considered as an attractive indirect method for CO₂ fixation (Scheme 1b).¹³

Diacids such as succinic acid derivatives are important core structures of many bioactive molecules and useful monomers for polymers.¹⁴ The production of diacids using CO₂ as the carboxyl source is a sustainable strategy, but only limited methods have been developed to date.¹⁵ Traditionally, electrochemical dicarboxylation of alkenes with CO₂ has been investigated, but these processes generally require a sacrificial anode.^{15,16} In addition, Martin and co-workers reported a Ni-catalyzed site-selective dicarboxylation of 1,3-dienes with CO₂, which used stoichiometric Mn as the reductant.¹⁷ In 2021, the group of Yu reported an elegant dicarboxylation of alkenes with CO₂ *via* a sequential single electron transfer (SSET) process, in which the reduction of the alkene substrate to a radical anion intermediate was the key step.¹⁸ Recently, the same group



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Scheme 1 The development of dicarboxylation of alkenes with formate and CO₂.



disclosed a remote dicarboxylation of alkene and benzylic C(sp³)-H bond *via* an intramolecular HAT.¹⁹ However, amine terminal reductants were necessary for these two transformations. Given the challenge of direct CO₂ reduction^{3,15,20} and the low cost of the formate salt that possessed a dual role in our preliminary results of dicarboxylation (Scheme 1a and b),² we envisioned using the formate for alkene dicarboxylation to obtain diacids in a redox-economical and practical manner.²¹

Herein, we report a visible-light-induced dicarboxylation of diverse alkenes with CO₂ using formate as a low-cost reductant and part of the carboxyl source. Notably, simple styrenes were well tolerated, and the reaction could be performed under mild conditions at ambient temperature and pressure of CO₂. Importantly, the highly competing hydrocarboxylation side reaction was successfully overridden.

Results and discussion

Our investigation began with using 1,1-diphenylethylene (**1a**) as the model substrate, which was treated with 30 W blue LED irradiation in the presence of a PC and an atmospheric pressure of CO₂ (Table 1). After extensive investigation of the reaction conditions, the desired dicarboxylation product **2a** was

Table 1 Optimization of reaction conditions^a

Entry	Deviations from standard conditions	2a yield [%]	2a_H yield [%]
1	None	91% ^b	—
2	In the dark	—	—
3	w/o 3DPAFIPN	—	—
4	w/o HCOOK	—	—
5	w/o DABCO	32%	28%
6	w/o CO ₂ (N ₂ atmosphere)	—	76%
7	w/o K ₃ PO ₄	40%	12%
8	w/o Cs ₂ CO ₃ ; K ₃ PO ₄ (3 equiv.)	44%	50%
9	w/o Cs ₂ CO ₃ and K ₃ PO ₄	11%	66%
10	HCOONa instead of HCOOK	70%	—
11	Quinuclidine instead of DABCO	40%	—
12	4DPAIPN instead of 3DPAFIPN	65%	—
13	4CzIPN instead of 3DPAFIPN	39%	—
14 ^c	[Ir(ppy) ₂ (dtbbpy)]PF ₆	7%	—
15	3DPAFIPN (2.0 mol%)	70%	—
16	3DPAFIPN (4.0 mol%)	86%	—
17	THF instead of DMSO	16%	—
18	DMA instead of DMSO	17%	—

^a Reaction conditions: **1a** (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Yield was determined by ¹H NMR with CH₂Br₂ as the internal standard. ^b Isolated yield was 88%. ^c [Ir(ppy)₂(dtbbpy)]PF₆ (5 mol%). 3DPAFIPN = 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile; DABCO = triethylenediamine.

generated in an 88% isolated yield using 3DPAFIPN as the PC in the presence of the HAT catalyst DABCO with HCOOK as the terminal reductant and Cs₂CO₃ and K₃PO₄ as the cooperative bases in DMSO at ambient temperature (entry 1).²² No product was found in the absence of either visible light or the PC, indicating the reaction was a photocatalytic reaction (entries 2 and 3). Importantly, HCOOK was essential for the reaction (entry 4). Surprisingly, in the absence of DABCO, a modest yield of the desired product **2a** was obtained along with some hydrocarboxylation side-product **2a_H**, suggesting that more than one HAT process might be involved in this reaction (entry 5). Interestingly, only the hydrocarboxylation product was obtained under a nitrogen atmosphere without adding CO₂ (entry 6), suggesting that HCOOK was also one of the carboxyl sources. Moreover, the addition of suitable bases was important to achieve a high yield of the desired product (entries 7–9, also see ESI† for screening of other bases) and avoid the generation of hydrocarboxylation side-product **2a_H** as well (entry 9), possibly by inhibiting direct protonation of the benzylic anion of the reaction intermediate. Other formates such as HCOONa were also used, but they were less effective than HCOOK (entry 10). Other HAT catalysts such as quinuclidine were also evaluated, but they were inferior to DABCO (entry 11).²³ Other PCs such as 4DPAIPN, 4CzIPN and [Ir(ppy)₂(dtbbpy)]PF₆ were also tested, but worse results were obtained (entries 12–14, also see ESI† for more PC structures). The exact reason for the disparity in photocatalyst performance is not clear at present. One possible reason for this might be that 3DPAFIPN has a strong reduction potential ($E_{\text{red}}(\text{PC}^*/\text{PC}^{\cdot-}) = -1.59 \text{ V vs. SCE}$ in MeCN for 3DPAFIPN) to facilitate the reduction of the benzylic radical of the reaction intermediate.²⁴ In addition, lower yields were delivered while reducing the loading of 3DPAFIPN (entries 15 and 16). Finally, DMSO was the best solvent of all those used such as THF and DMA (entries 17 and 18).

With the optimized reaction conditions in hand, we first examined this protocol with a variety of 1,1-disubstituted ethylenes (Table 2). Good to excellent yields of desired dicarboxylation products were obtained with model substrate **1a** and mono- or di-substituted 1,1-diarylethylenes bearing a list of functional groups at *ortho*-, *meta*- or *para*-positions of the phenyl groups (**2a–2k**). Notably, a 6 mmol scale reaction with **1a** also provided 85% yield of desired product. It is worth mentioning that it is generally recommended to set up the reaction by weighing the chemical in a glovebox to reduce the possible hydrocarboxylation side product, but setting-up the reaction outside the glovebox could also deliver similar results (89% yield with **1a**) if the reactants were kept anhydrous (see ESI†). Both electron-donating methyl (**2b**, **2d**, **2f**, and **2g**) and methoxy (**2h**, **2i**, and **2k**) substituents and electron-withdrawing fluoro (**2c** and **2j**) and trifluoromethyl (**2e**) ones were tolerated. Moreover, heteroaryl containing substrates were also compatible with this method, though lower yields were obtained (**2l–2n**). Other di-substituted ethylenes (**2o**, **2p**, and **2q**) and even a tri-substituted one (**2r**) were also viable to deliver acceptable yields of products. Note that the reaction with a diene substrate (**1s**) would give both 3,4-dicarboxylation and 1,4-dicarboxylation products. In addition, good results were obtained with



Table 2 Scope of 1,1-disubstituted ethylenes and acrylates^a

^a Reaction conditions: 1 (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. ^b Yield of 6 mmol scale reaction (52 h). ^c The product was methylated with SOCl₂/MeOH before isolation. ^d Major product 3,4-dicarboxylation product (2s_a, 37%) displayed; minor product: 1,4-dicarboxylation product (2s_b, 17%).

methacrylates (2t and 2u), although only a modest yield was obtained with a 2-benzylacrylate (2v). Of note, only the hydrocarboxylation product was isolated with an acrylamide substrate such as 2-benzyl-*N*-methyl-*N*-phenylacrylamide.

We then moved on to investigate the scope of the more challenging simple styrenes, leading to generally good yields with a variety of substituted styrenes regardless of the electronic properties and the position of the substituent on the aromatic

ring. It should be noted that in Zhu's work, only a very narrow scope of simple styrenes were tolerated with low yields.²² As shown in Table 3, the un-substituted styrene 3a and the *ortho*-substituted styrenes with electron-donating methyl (3b) and methoxyl (3c) groups proceeded smoothly and gave good yields of the desired products. Notably, the yield of 4c could be increased to 94% by slightly elevating the reaction temperature to 40–45 °C. Moderate yield was obtained with substrate 3d

Table 3 Scope of simple styrenes^a

^a Reaction conditions: 3 (0.2 mmol), 3DPAFIPN (6.2 mol%), DABCO (0.06 mmol), Cs₂CO₃ (0.6 mmol), K₃PO₄ (0.4 mmol), HCOOK (0.6 mmol) in DMSO (2 mL), 1 atm CO₂, 30 W blue LEDs, rt (25–33 °C), 24 h; then treated with 2 mL of HCl (2 N). Isolated yields. ^b Reaction temperature: 40–45 °C. ^c Desired product displayed; de-chlorination product (18% for 4d, 16% for 4f) not shown. ^d About 6% hydrocarboxylation side product. ^e The product was methylated with SOCl₂/MeOH before isolation.



bearing an *ortho*-chloro group, since some de-chlorination occurred. In addition, both electron donating (**4e**) and withdrawing (**4f** and **4g**) groups were well tolerated at the *meta*-position. Good results were also obtained with substrates containing several representative substituents at the *para*-position of the phenyl ring (**4h–4l**). Finally, heteroaryl containing substrates were also tested, but the yields were much lower (**4m** and **4n**). It is noteworthy that the hydrocarboxylation side product was not detected or only in trace amounts, and only substrate **3g** led to 6% of the hydrocarboxylation side product.

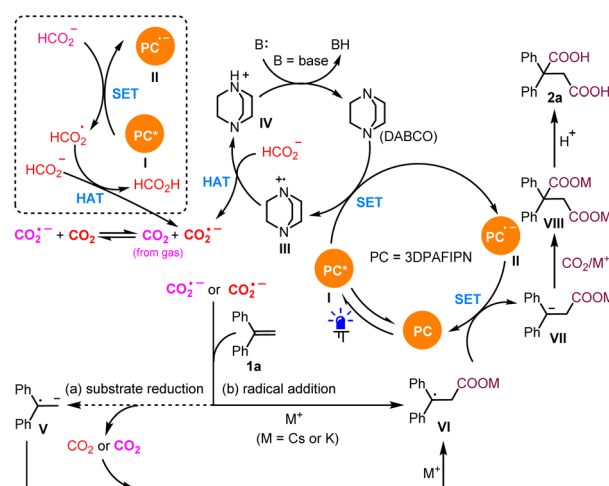
To obtain insights into the reaction mechanism, several control experiments were then carried out (Scheme 2). Ring-opening product **6** was afforded in the radical clock experiment, indicating a benzyl radical might be generated after $\text{CO}_2^{\cdot-}$ addition to the alkene (Scheme 2a). When the reaction was run in the presence of D_2O , hydrocarboxylation product **2a_{H-DH}** was produced instead of dicarboxylation with traces of reduction product **2a_{HHH}**, indicating the formation of a benzylic anion intermediate and that the formation of anions at the alkene terminal position was trivial (Scheme 2b(i)). Similar results were obtained when the reaction was carried out without the addition of CO_2 gas (Scheme 2b(ii)). The low deuteration ratio at the benzylic position in these two reactions (49% and 32%,



Scheme 2 Mechanistic study experiments and product application.

respectively) might suggest that a HAT process between the benzylic radical and formate was also involved except the protonation of the benzylic anion under current reaction conditions. In addition, four possible dicarboxylation products were obtained when using ^{13}C -labelled formate (*i.e.* commercially available $\text{H}^{13}\text{COONa}$),²⁵ suggesting that formate was also part of the carboxyl source (Scheme 2c). Moreover, no carboxylation products were detected when the reaction was performed using a stoichiometric amount of **DABCO** without formate, indicating that the reduced **3DPAFIPN** could not reduce the substrate **1a** or CO_2 to initiate the reaction (Scheme 2d). Furthermore, the Stern–Volmer quenching experiments showed that the activated catalyst (**PC***) was mainly quenched by **DABCO**, but it could also be slightly quenched by **HCOOK** (see ESI†). Finally, a one-step procedure was developed for the synthesis of nervous system drug phensuximide (Scheme 2e) to demonstrate the application of the dicarboxylation product.

Based on the above mechanistic studies, a possible catalytic cycle was proposed (Scheme 3). Upon blue light irradiation, the excited **PC*** (**I**) is generated and then quenched by **DABCO** to form **PC⁻** (**II**) ($E_{1/2}(\text{PC}^*/\text{PC}^-) = +1.09$ V vs. SCE in MeCN)²⁴ and the radical cation of **DABCO** (**III**). A HAT between radical **III** and HCO_2^- produces $\text{CO}_2^{\cdot-}$ and cation **IV**. Alternatively, $\text{CO}_2^{\cdot-}$ can be partially generated by a HAT process between HCO_2^- and HCO_2^{\cdot} that is produced by reducing **PC*** with HCO_2^- ($E_{\text{ox}}(\text{HCO}_2^-/\text{HCO}_2^{\cdot}) = +1.25$ V vs. SCE),^{4b} considering the results of Stern–Volmer quenching experiments with formate (see Fig. S5† of SI) and the fact that some product could be obtained without **DABCO** (see entry 5 in Table 1). Subsequently, $\text{CO}_2^{\cdot-}$ may reduce the substrate ($E^0 = -2.25$ V vs. SCE for **1a**)²⁶ to give radical anion **V**, considering that product **2a** was the major product in the ^{13}C -labelling experiment of Scheme 2c. However, the direct addition of $\text{CO}_2^{\cdot-}$ to the double bond of **1a** to afford intermediate **VI** is more likely based on the results in Scheme 2b. In this scenario, a potential facile electron transfer/equilibration between $^{13}\text{CO}_2^{\cdot-}$ and the excess CO_2 gas may account for the observation of **2a** as the main product in Scheme 2c.²⁷ Moreover, since the reduction of simple styrenes ($E_{1/2} = -2.58$ V vs. SCE in



Scheme 3 Proposed catalytic cycle.



DMF for **3a**)²⁸ is more demanding than **1a**, direct CO₂^{•-} addition is possibly the predominant pathway for substrates in Table 3. The radical intermediate **VI** was then reduced by PC^{•-} (**II**) to give the anion **VII**, which undergoes nucleophilic attack of CO₂ to afford the final product **2a** after acidification of the salt intermediate **VIII**.

Conclusions

In conclusion, we have developed a visible-light-driven alkene dicarboxylation using formate and CO₂, overriding the highly competing hydrocarboxylation side reaction successfully. Good yields of products were obtained with diverse alkenes including simple styrenes under mild reaction conditions at ambient temperature. The dual role of the low-cost formate as a reductant and the C1 source may open up the discovery of a range of new transformations including indirect utilization of CO₂ under mild and friendly conditions.

Data availability

Experimental procedures, characterisation data, and NMR spectra for new compounds can be found in the ESI.†

Author contributions

F. Zhang performed the experiments and developed the method. X. Wu, P. Gao and S. Ai prepared some of the substrates and catalyst. H. Zhang and Z. Li repeated and checked the results of some of the reactions. G. Li conceived the method, directed the project and wrote the manuscript with the feedback from the other authors.

Conflicts of interest

There are no conflicts to declare.

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