

Double Hydrogen Atom Transfer Strategy for Catalytic Acceptorless Dehydrogenation of Cycloalkanes

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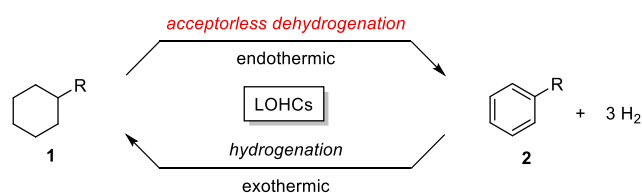
Supporting Information Placeholder

ABSTRACT: The advancement of an effective hydrogen liberation technology from liquid organic hydrogen carriers (LOHCs), such as cyclohexane and methylcyclohexane (MCH), holds significance in realizing a hydrogen-centric society. However, the attainment of homogeneous catalytic acceptorless dehydrogenation (CAD) characterized by elevated selectivity for thorough aromatization under mild conditions remains unrealized. In this study, a catalyst system, facilitated by a double hydrogen atom transfer (HAT) processes, has been devised for the CAD of inert cycloalkanes at ambient temperature under visible light irradiation. Through the synergistic utilization of tetrabutylammonium chloride (TBACl) and thiophosphoric acid (TPA) HAT catalysts, successful CAD with comprehensive aromatization has been accomplished with high functional group tolerance.

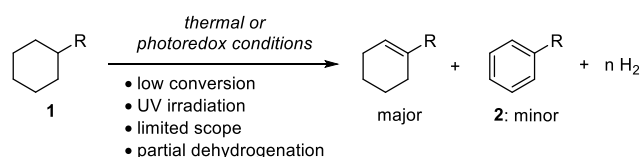
Contributions to the hydrogen economy through sustainable approaches are increasingly imperative for delineating the trajectory of a future clean energy supply.¹ Within the context of green energy, hydrogen gas has emerged as the optimal alternative to meet the demands of energy supply. However, the current infrastructure grapples with the significant challenge of hydrogen storage and transport due to its low density. The adoption of liquid organic hydrogen carrier (LOHC) technology provides a safe and efficient means of storing and transporting hydrogen gas with heightened density, achieved through catalytic acceptorless dehydrogenation (CAD) and the hydrogenation of small organic molecules.² Prominent among these LOHCs are liquid cyclic alkanes such as cyclohexane and methylcyclohexane (MCH), exhibiting promising hydrogen storage capacities of up to 7.2 wt% and 6.2 wt%, respectively (Scheme 1a).^{3,4} Nevertheless, dehydrogenation of these inert alkanes, characterized by intrinsically stable sp³ C–H bonds with a bond dissociation energy (BDE) of ~100 kcal/mol and a pK_a of ~40, proves to be endothermic and often necessitates high reaction temperatures (>150 °C). The predominant study

of CAD for simple alkanes employs homogeneous pincer metal complexes at elevated temperatures, leading to substantial energy consumption.^{5,6,7} The lack of selectivity in terms of regio-, chemo-, and degree-of-dehydrogenation, coupled with high temperature-induced catalyst deactivation, is a significant concern (Scheme 1b).⁸

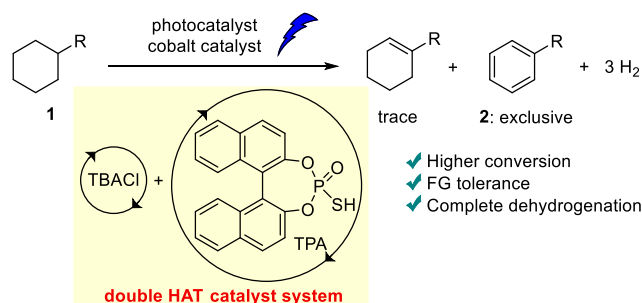
(a) Hydrogenation/dehydrogenation cycle for LOHC application



(b) Previous CAD reactions



(c) Current work



Scheme 1. Catalytic acceptorless dehydrogenation of cyclohexane derivatives.

In tandem with thermal dehydrogenation, there has been a surge in photoinduced CAD. This approach has the potential to overcome thermodynamic limitations and facilitate reactions under milder conditions.^{9,10} Pioneering CAD under UV irradiation, Crabtree successfully monodehydrogenated cyclooctane to cyclooctene using an Ir catalyst.¹¹ Subsequent developments by Saito, Tanaka, and Goldman extended CAD of alkanes under UV irradiation using a Rh complex.¹² Beller enhanced the efficiency of the Rh complex for CAD of various alkanes.¹³ Despite these advancements, the utilization of a UV light source and the associated poor regioselectivity impose limitations on these approaches. In 2015, Sorensen and colleagues reported CAD of alkanes under near-UV light irradiation, employing a cobaloxime catalyst and tetrabutylammonium decatungstate (TBADT) photocatalyst.¹⁴ Although CAD was achieved at room temperature, the process was confined to monodehydrogenation of cycloalkanes such as cyclohexane, exhibiting low catalytic activity (up to a 19% yield). Huang and Xu further refined this system by incorporating a cobalt complex catalyst and a 2-chloroanthraquinone catalyst.¹⁵ Nevertheless, yield and degree-of-dehydrogenation selectivity for simple alkane substrates remained inefficient. Additionally, the method was mostly studied for benzylic or activated C–H bonds with smaller BDEs. To date, there is no example of complete dehydrogenation of cycloalkanes to the corresponding aromatic derivatives using homogeneous catalysts, posing a significant challenge when contemplating applications to LOHC. We here disclose a dual hydrogen atom transfer (HAT)-enabled multi-catalyst system, facilitating the complete dehydrogenation of unactivated cycloalkanes at room temperature under visible light irradiation (Scheme 1c).

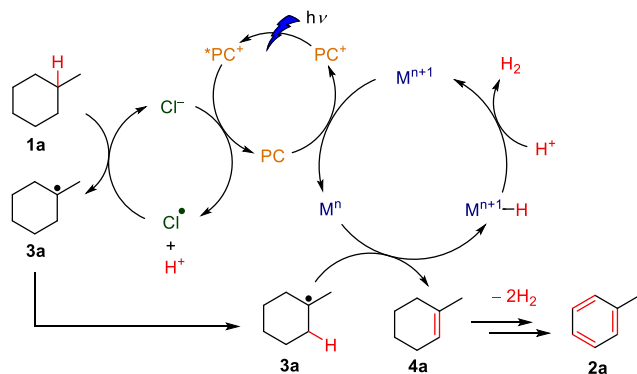


Figure 1. Proposed reaction mechanism

At the outset of our studies, we envisioned developing a ternary catalyst system¹⁶ consisting of a highly active HAT catalyst that can cleave a stable C–H bond of alkanes (e.g., **1a**), such as a chlorine radical generated through single electron oxidation of chloride by a photoredox catalyst (PC⁺; Figure 1). Visible light irradiation of PC⁺ generates a long-lived photoexcited state (*PC⁺), which oxidizes chloride to produce a HAT active chlorine radical (Cl[•]). The chlorine radical abstracts a hydrogen atom from **1a**, generating alkyl radical **3a**. Then, a metal complex (Mⁿ) intercepts **3a** and undergoes β-hydride elimination to generate metal hydride species (Mⁿ⁺¹–H), which upon protonolysis releases molecular hydrogen. Single electron reduction of the metal complex catalyst (Mⁿ⁺¹) by the reduced form of photoredox catalyst (PC) closes the catalytic cycle. Repeating this sequence twice from intermediate alkene **4a** produces toluene (**2a**), evolving, in total, three equivalents of hydrogen gas from **1a**.

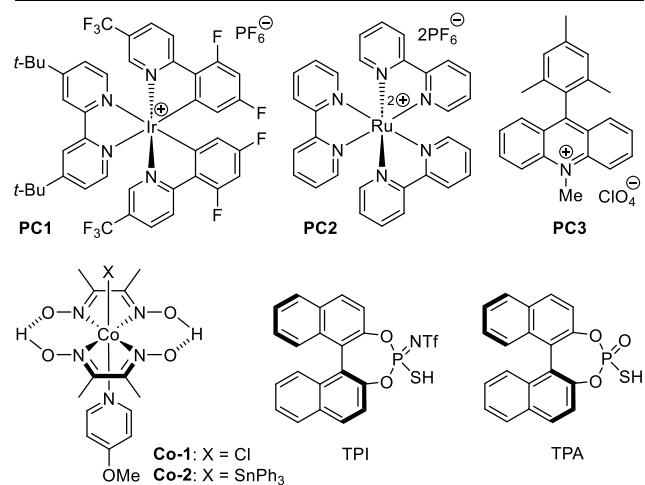
We chose MCH (**1a**) as a model substrate for the reaction optimization due to its recognized ability to serve as a LOHC. Employing tetrabutylammonium chloride (TBACl) and PC1 as a chlorine radical-forming catalyst combination,¹⁷ we first studied several metal complex catalysts (Table 1, entries 1–3). Cobaloxime catalyst¹⁸ **Co-1** produced trace amounts of dehydrogenation products **2a** and **4a** (entry 3). Benzene was found to be the best solvent, affording a regioisomeric mixture of alkenes **4a** containing methylenecyclohexene, 1-methyl-1-cyclohexene, and 1-methyl-4-cyclohexene in 14% combined yield and 3% of toluene (**2a**) (entry 4). The use of other photoredox catalyst instead of PC1 was detrimental (entries 5 and 6).

Table 1. Optimization of Reaction Conditions

[M] (2.5 mol%), PC1 (1 mol%)
HAT-1 (5 mol%)
HAT-2 (1.25 mol%)
additive (30 mol%)

solvent, blue LED, 24 h

entry	[M]	HAT		additive	solvent	yield (%) ^a	
		1	2			2a	4a
1	Pd(BF ₄) ₂ ^b	TBACl	–	–	DCM	ND	ND
2	Ni(NTf ₂) ₂ ^c	TBACl	–	–	DCM	ND	ND
3	Co-1	TBACl	–	–	DCM	trace	trace
4	Co-1	TBACl	–	–	PhH	3	14
5	Co-1 ^d	TBACl	–	–	PhH	2	ND
6	Co-1 ^e	TBACl	–	–	PhH	2	trace
7	Co-1	TBACl	TPA	–	PhH	14	trace
8	Co-1	TBACl	TPI	–	PhH	6	9
9	Co-1	TBACl	TPA	py	PhH	36	trace
10	Co-1	TMACl	TPA	py	PhH	15	trace
11	Co-1	TEACl	TPA	py	PhH	13	trace
12	Co-1	TBABr	TPA	py	PhH	trace	trace
13	Co-1	TBAI	TPA	py	PhH	trace	trace
14 ^f	Co-1	TBACl	TPA	py	PhH	58	trace
15	Co-1 ^g	TBACl	TPA	py	PhH	ND	ND
16	–	TBACl	TPA	py	PhH	ND	ND



^aDetermined by GC analysis using decane as an internal standard. ^bPd(BF₄)₂•4MeCN was used. ^cNi(NTf₂)₂•xH₂O was used. ^dPC2 was used instead of PC1. ^ePC3 was used instead of PC1. ^fAfter 16 h, another set of the catalysts was added, and the reaction was continued for a further 16 h. ^gWithout PC.

Although improvement in dehydrogenation was observed (entry 4), the selectivity was poor toward fully dehydrogenated

product **2a**. Thus, we considered incorporating a second HAT catalyst effective for alkene intermediates **4a**. The use of 1.25 mol% TPA¹⁹ successfully switched the selectivity towards **2a**, providing a 14% yield (entry 7). Other HAT catalysts did not promote full dehydrogenation, showcasing the superiority of TPA (entry 8 and Table S2.3).

Despite the significant achievement of complete dehydrogenation selectivity, yield was still low. The unsatisfactory reactivity was likely due to the instability of the chlorine radical. To address this concern, we investigated additives to stabilize the chlorine radical, especially pyridines.²⁰ The screening of different amounts of pyridine as an additive was carried out (Table S2.4) and it was observed that 30 mol% pyridine (py) dramatically increased yield of **2a** to 36% with the generation of **4a** in trace amounts (Table 1, entry 9). We then screened sterically and electronically distinct pyridine derivatives (Table S2.5) and concluded that the unsubstituted pyridine was the best choice. Further screening of different substituents on the cobaloxime catalyst was performed (Table S2.6). Among those screened, **Co-1** was found to be superior. Next, we investigated different halide sources. The use of Me₄NCl (TMACl) or Et₄NCl (TEACl) provided 15% or 13% of **2a**, respectively (entries 10 and 11), whereas the employment of Bu₄NBr (TBABr) and Bu₄Nl (TBAl) completely shut down the reaction (entries 12 and 13). These findings highlight the exceptional activity of a chlorine atom as a HAT catalyst. At this stage, we suspected the decomposition of catalyst components over time. To enhance the reactivity, we examined the two-portion addition of the catalyst system. The addition of the catalyst set after 16 h and allowing the reaction to continue for a further 16 h led to an increase in yield to 58% (entry 14). Control experiments showcased that the use of the photoredox and cobaloxime catalysts is critical for the reaction progress (entries 15 and 16).

Under the optimized conditions, we explored the substrate scope as illustrated in Table 2. Applying the optimized conditions to cyclohexane (**1b**) in PhCl solvent produced benzene (**2b**) in only 9% yield (Table S2.7). We found that slight modifications of the optimized conditions to using a **Co-2** catalyst²¹ and a 3-phenyl pyridine (3-Ph-py; Table S2.8) additive afforded **2b** in a higher 68% yield. Similarly in this case, no alkene products **4b** were observed. The reaction proceeded smoothly when substituents with considerable steric hindrance were introduced (**2c-2e**). This system can be employed for scaling up the reaction without significantly compromising reaction efficiency (**2e**, 55%). Cyclohexane derivatives incorporating a boronate ester (**1f**), methoxy (**1g**), methyl ester (**1h**), and cyano group (**1i**) produced the corresponding aromatic products (**2f-2i**). Furthermore, the reaction successfully proceeded with substrates containing two or three cyclohexane moieties (**1j-1p**), either fused or linked, affording the corresponding aromatized products. Notably, the reaction involving perhydropyrene (**1p**) cleanly furnished pyrene (**2p**), albeit in moderate yield of 22%.

Table 2. Substrate Scope^a

substrate 1	product 2	substrate 1	product 2
1a	2a : 58%	1k	2k : 59%
1b	2b : 68% ^b	1l	2l : 35% ^b + 2l' : 10% ^b
1c	2c : 60%	1m	2m : 71% + 2m' : 14%
1d	2d : 73%	1n	2n : 42%
1e	2e : 76%, 55% ^c	1o	2o : 42% + 2o' : 11%
1f	2f : 51%	1p	2p : 22%
1g	2g : 64%		
1h	2h : 64%		
1i	2i : 40%		
1j	2j : 38% ^b		

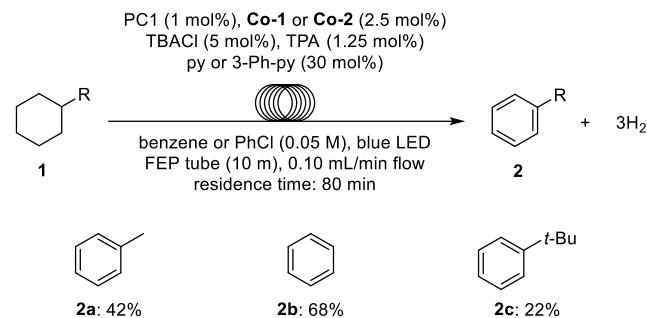
^aGeneral procedure: **1** (0.20 mmol), PC1 (0.0020 mmol), **Co-1** (0.0050 mmol), TBACl (0.010 mmol), TPA (0.0025 mmol), and pyridine (0.060 mmol) were reacted in benzene (4 mL) at room temperature under blue LED irradiation for 18 h. After filtration through a short pad of silica gel, this process was repeated.

^bThe reaction was conducted using **Co-2** and 3-Ph-py in PhCl.
^c1.0 mmol scale.

Next, we attempted to enhance the efficiency of the reaction through a continuous-flow approach.²² The continuous-flow system holds a potential to augment the reactivity of photoredox reactions by optimizing light irradiation efficiency and facilitating the efficient removal of hydrogen gas from the system. In this context, we explored the application of a continuous-flow setup using fluorinated ethylene-propylene (FEP) tubes for the photoredox reaction (Scheme 2). Notably, the conversion of **1a** to **2a** reached 42% within 80 min. Employing **1b** yielded **2b** in 68% yield. These findings indicate that the continuous-flow reaction system approaches the efficiency of the

two-portion catalyst addition process in batch (Table 2). However, yield of **2c** was limited to 22%, prompting further exploration of more intricate reaction conditions for certain substrates to potentially enhance the yield.

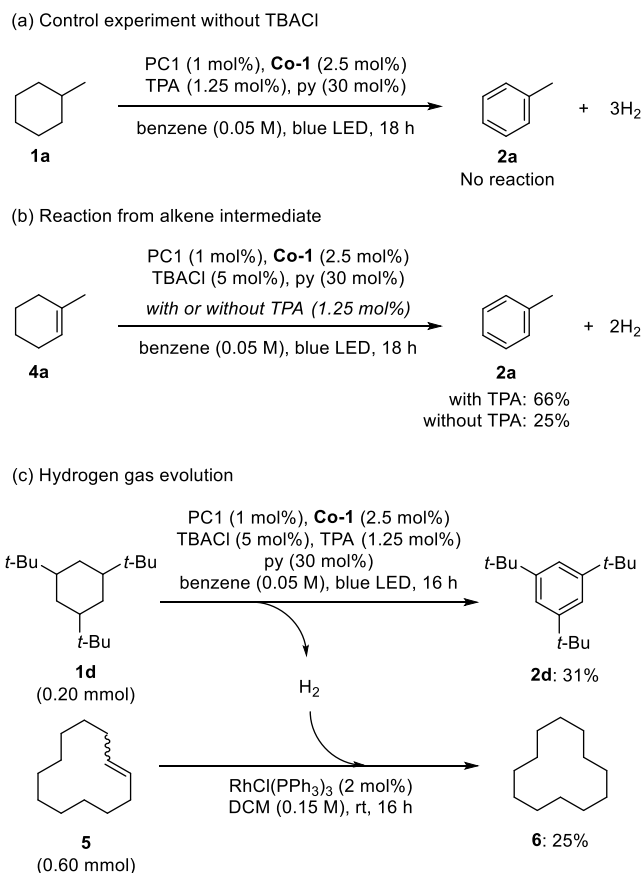
Scheme 2. Application to Continuous Flow System^a



^aFor **1a** and **2c**, Co-1, py, and benzene were used. For **2b**, Co-2, 3-Ph-py, and PhCl were used.

To gain preliminary insights into the reaction mechanism, a series of experiments were conducted (Scheme 3). To elucidate individual roles of the two HAT catalysts, the dehydrogenation reaction of **1a** was investigated without TBACl (Scheme 3a). The reaction failed to proceed, indicating that the dehydrogenation of alkanes necessitates the generation of a chlorine radical. EPR measurements and transient absorption spectroscopy supported the generation of a chlorine radical, which subsequently cleaves a C–H bond of **1a** (Figures S1–S7). In dehydrogenation of alkene **4a**, a notable difference in reactivity was observed depending on the presence or absence of TPA (Scheme 3b, 66% vs. 25%). This observation suggests that the TPA radical serves as a HAT catalyst, facilitating dehydrogenation from alkene intermediates. We postulate that the two HAT catalysts coexist (Figure S3) and operate independently to enable complete dehydrogenation, although further detailed studies are required to elucidate the double HAT mechanism. Lastly, to verify the release of hydrogen gas, a two-pot transfer hydrogenation was conducted (Scheme 3c). The result supported that the desaturation was at least mainly due to the evolution of hydrogen gas.

Scheme 3. Mechanistic Insights



In conclusion, we have achieved the first homogeneous complete CAD of promising LOHC candidates, specifically cyclohexane derivatives, utilizing visible light irradiation at room temperature. The pivotal factor contributing to this success is the synergistic combination of dual HAT catalysts, namely TBACl and TPA, facilitating aromatization. The chlorine radical catalysis is essential for the first HAT from the alkanes, and the TPA radical HAT catalysis ensures subsequent complete dehydrogenation from alkene intermediates. This represents an entry to leveraging such a synergistic effect through the combination of distinct HAT catalysts. The applicability of this reaction extends to various cyclohexane derivatives, demonstrating smooth progression even in a continuous flow reaction setup. Further enhancing reactivity and expanding the generality of this methodology are ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Synthetic protocols, experimental details and NMR charts (PDF).

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Notes

The authors declare no competing financial interest.

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