Photocatalysis

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Towards a Practical Development of Light-Driven Acceptorless Alkane Dehydrogenation**

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Abstract: *The efficient catalytic dehydrogenation of alkanes to olefins is one of the most investigated reactions in organic synthesis. In the coming years, an increased supply of shorter-chain alkanes from natural and shale gas will offer new opportunities for inexpensive carbon feedstock through such dehydrogenation processes. Existing methods for alkane dehydrogenation using heterogeneous catalysts require harsh reaction conditions and have a lack of selectivity, whereas homogeneous catalysis methods result in significant waste generation. A strong need exists for atom-efficient alkane dehydrogenations on a useful scale. Herein, we have developed improved acceptorless catalytic systems under optimal light transmittance conditions using trans-*$[Rh(PMe_3)_2(CO)Cl]$ *as the catalyst with different additives. Unprecedented catalyst turnover numbers are obtained for the dehydrogenation of cyclic and linear (from* C_4*) alkanes and liquid organic hydrogen carriers. These reactions proceed with unique conversion, thereby providing a basis for practical alkane dehydrogenations.*

Olefins are a fundamental and versatile feedstock in the chemical industry but unfortunately they are much less naturally abundant than alkanes.[1,2] Industrial olefins are usually prepared by hydrocarbon cracking from raw materials such as natural gas condensate or petroleum-distilled naphtha derivatives. However, the harsh reaction conditions required for such processes (700–900 °C) limit their applicability in terms of direct further synthetic manipulation.[3] According to the *2013 Annual Energy Outlook* report from the U.S. Department of Energy,[4] petrochemical companies have announced their intention to use alkanes directly as olefin feedstock through in situ dehydrogenation because of the increased alkane supply from natural gas and shale gas processing plants.[4,5] In this context, acceptorless dehydrogenation of alkanes is emerging as an atom-economical and environmentally benign synthetic route.[1]

Although hydrogen generation from saturated hydrocarbons is entropically favored, it is thermodynamically disfavored as it is a highly endothermic process. The cracking of saturated hydrocarbons is thermodynamically favored (C–C: 246 $kJ\,mol^{-1}$) compared to dehydrogenation (C–H: 363 $kJ\,mol^{-1}$), which often leads to C–C bond rupture at higher temperature. This issue is one of the inherent limitations of heterogeneous dehydrogenation catalysts, in addition to catalytic deactivation and a lack of selectivity.[3] In principle, alkane dehydrogenation can be performed at lower temperatures (150–250 °C) under homogeneous conditions.[6–13] However, an excess of sacrificial alkene is commonly employed as the hydrogen acceptor to compensate for the high endothermicity. These reactions consequently lead to the stoichiometric generation of unwanted by-products.[2,6–9] Current transfer-dehydrogenation processes use thermally stable sophisticated iridium pincer complexes such as those described by the groups of Goldman,[2,7] Brookhart,[8] and Jensen.[9] Unfortunately, the potential application of these thermal dehydrogenation processes is limited because of the presence of the hydrogen acceptor, activity inhibition from the olefin, high reaction temperatures, and long reaction times. Alternatively, in acceptorless alkane dehydrogenation, removal of molecular hydrogen from the system is essential to shift the equilibrium toward the desired products.[1,2,10–12] To avoid the use of an alkene as an acceptor and to carry out the reaction at a lower temperature, photocatalytic approaches based on the use of light as a "green reagent" have been proposed as an environmentally benign option for alkane dehydrogenation.[14] The first example in this area was reported by the research group of Crabtree in 1985 by using $[IrH_2(CF_3CO_2)(PR_3)_2]$($R{=}C_6H_4F$-*p* and C_6H_{11}) as the catalyst.[10a] Dehydrogenation of cyclooctane to cyclooctene proceeded with a turnover number (TON) of 7 after seven days. Nomura and Saito subsequently demonstrated that Vaska-type rhodium complexes $[RhCl(CO)(PR_3)_2]$ (R = Me, Et, and Ph) gave improved activity.[11] Goldman and coworkers later improved this method for alkane dehydrogenation by using cycloalkanes as the substrate.[12]

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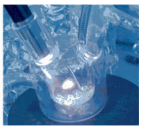
Despite continued research in the field of homogeneous thermal dehydrogenation of alkanes over the last 30 years,[2,6–10] relatively little progress has been made in photochemical dehydrogenation. Herein, we present a new procedure for an atom-economical alkane dehydrogenation process, in which [Rh(PMe$_3$)$_2$(CO)Cl] is used as the catalyst. This method is carried out in the presence of specific additives and under optimal conditions for light transmittance. The method allows for significantly enhanced catalyst turnover numbers and the possibility to dehydrogenate various alkanes, including potentially liquid organic hydrogen carriers (LOHC), on a practical scale.

In the initial model system, *n*-octane was irradiated with a conventional mercury vapor lamp (460 W Philips) in the presence of [Rh(PMe$_3$)$_2$(CO)Cl] as catalyst in a standard round bottom flask. Unfortunately, deactivation of the catalyst rapidly occurred to form rhodium black. This prompted us to use a more controlled 150 W Lumatec device and a specifically designed three-necked glass photoreactor for subsequent investigations. Previous reports on the photochemical dehydrogenation of alkanes demonstrated the importance of Rh−CO bond photolysis to generate a highly reactive tricoordinate rhodium(I) complex. To improve the stability of the active catalyst and to facilitate an enhanced interconversion of light to chemical energy, the influence of photosensitizers and/or stabilizing reagents as additives was studied (Table 1; Supporting Information, Table S1). In the absence of additives, a mixture of octenes with a catalyst TON of 333 was achieved after 3 h. To our surprise, of the additives screened, only 2,2′-bipyridine and 4,4′-bipyridine had a positive influence on the activity. A TON of 489 was achieved after a reaction time of 5 h when 4,4′-bipyridine was used as an additive (Table 1; entry 5). Importantly, no reaction is observed with protected bipyridine (4,4′-bipyridine·2 RCl, R = H, CH$_3$), thus demonstrating the influence of free base in this catalysis (Table 1; entries 6 and 7).

Table 1: Catalytic dehydrogenation of *n*-octane in the presence of a [Rh(PMe$_3$)$_2$(CO)Cl] catalyst: Initial screening of additives.[a]

$$\underset{(30\text{ mmol})}{n\text{-Octane}} \xrightarrow[h\nu\ (\lambda=320\text{-}500\text{ nm})]{\substack{[\mathrm{RhCl(CO)(PMe_3)_2}]\ (0.004\text{ mmol})\\ +\ \text{Additive}\ (0.02\text{ mmol})}} \text{Octenes}$$



Entry	Additive	*t* [h]	TON	TOF [h^{-1}]
1	–	3	333	111
2	2,2′-bipyridine	3	419	140
3	4,4′-dimethyl-2,2′bipyridine	3	236	79
4	4,4′-bipyridine	3	411	137
5	4,4′-bipyridine	5	489	99
6	4,4′-bipyridine·2 HCl	3	–	–
7	methyl viologen	3	–	–
8	2,2′-biquinoline	3	209	70
9	2,2′-bipyrimidine	3	264	66
10	bathocuproine	3	310	104
11	bathophenanthroline	3	149	50
12	phenanthroline	3	155	52
13	3,4,7,8-tetramethyl-1,10-phenanthroline	3	117	39
14	proton sponge	3	230	77
15	TiO$_2$	3	–	–
16	K$_2$S$_2$O$_8$	3	211	71

[a] Reaction conditions: [Rh(PMe$_3$)$_2$(CO)Cl] catalyst (1.30 mg, 0.004 mmol), the respective additive (0.02 mmol), and *n*-octane (5 mL, 30 mmol) were placed in a three-necked double-walled glass vessel. The reaction was carried out for the specified time under irradiation with light (λ = 320–500 nm) and constant stirring (1000 rpm) under a high stream of argon. The temperature was recorded within the region of 85–88 °C during the reaction. The TON was determined by GC with respect to isooctane as an internal standard. TON = [mmol of product]/[mmol of catalyst]; TOF (turn over frequency) = (TON/Time in h). See Table S1 for further optimization screening and the Supporting Information for experimental details.

Several photocatalysts were tested, but only [Rh(PMe$_3$)$_2$(CO)Cl] was found to be active under our conditions (Table S1). When [Rh(PMe$_3$)$_3$Cl] and [Ir(PMe$_3$)$_2$(CO)Cl] were used as catalyst, no conversion of octane was detected (Table S1; entries 28 and 29). This observation suggests a specific photocatalytic influence of the rhodium-carbonyl moiety towards alkane dehydrogenation and corresponds with the results of Goldman and co-workers.[12] Attempts to dehydrogenate *n*-octane in a metal reactor were unsuccessful. However, upon addition of glass beads to the reactor under similar conditions, traces of octenes were detected. This result might be explained by the Tyndall effect, namely an increased scattering of blue light in solution (Table S1; entries 26 and 27). We subsequently investigated the influence of the glass wall in the present photocatalytic method. The double-walled three-necked glass photoreactor was replaced by Schlenk tubes with different glass thicknesses. Indeed, as shown in Table 2, the light transmittance has a significant influence on the efficiency of the catalytic process and the product yield increased with decreasing glass thickness. The increased transmittance more effectively compensates the endothermic nature of alkane dehydrogenation. To our delight, a higher yield of octenes was achieved after a reaction time of 7 h using a Schlenk tube with glass walls of width 1.2 mm, which gave rise to a catalyst TON of 1518. These results represent the highest homogeneous catalyst turnover numbers achieved for a linear alkane dehydrogenation under such benign conditions, with or without acceptor. The increase in activity is attributed to the direct light irradiation. Note, in the three-necked photoreactor, the light source and reaction mixture were separated by an argon medium. To our knowledge, this is the first time that the influence of light transmittance has been investigated in photocatalytic reactions.

Measurements of the intensity of light transmittance reveal that there is a relationship between glass thickness and transmittance (Figure S1). As expected, we observed an increase of light transmittance (approx. 2 %) with a decrease of glass thickness from 3.0 mm to 1.4 mm. This effect was less pronounced than anticipated.

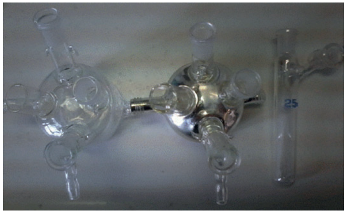
To prove the generality of the present photocatalytic method, reactions of 14 different linear (C$_4$–C$_{12}$) and cyclic alkanes including various LOHCs were evaluated (Table 3). Positive results were also obtained for the dehydrogenation of cyclooctane with our experimental set up and chosen coligand additive (Table S2). *cis*-Cyclooctene was obtained with an excellent catalyst TON of 2883.[15a] Similarly, catalyst TONs of 1200 and 975 were obtained for methylcyclohexane and cyclohexane, respectively.

Table 2: The influence of light transmittance on reaction with *n*-octane as substrate and $[Rh(PMe_3)_2(CO)Cl]$ as catalyst.[a]

$$n\text{-Octane (30 mmol)} \xrightarrow[h\nu\ (\lambda=320\text{-}500\ \text{nm})]{[RhCl(CO)(PMe_3)_2]\ (0.004\ \text{mmol}) + 4,4'\text{-bipyridine (0.02 mmol)}} \text{Octenes}$$

Entry	Glass vessel (wall width, mm)	*t* [h]	TON	TOF [h^{-1}]
1	photovessel (2.3)	5	489	99
2	mirrored photovessel (2.3)	5	636	127
3	Schlenk tube (3.0)	5	746	150
4	Schlenk tube (1.8)	5	1069	211
5	Schlenk tube (1.6)	5	1268	253
6	Schlenk tube (1.2)	5	1353	270
7[b]	Schlenk tube (1.2)	7	1518	217

[a] Reaction conditions: $[Rh(PMe_3)_2(CO)Cl]$ catalyst (1.30 mg, 0.004 mmol), 4,4′-bipyridine (0.02 mmol), and *n*-octane (5 mL, 30 mmol) were placed in a specified glass vessel. The reaction was carried out for the specified time under irradiation with light ($\lambda = 320$–500 nm) and constant stirring (1000 rpm) under a high stream of argon. The TON was determined by GC with respect to isooctane as an internal standard. [b] Product distribution: 1-octene (35 %), 2-octene (45 %; 35 % *trans* + 10 % *cis*), 3-octene (5 %), 4-octene (15 %), dienes (traces).

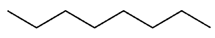
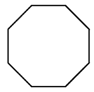
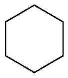
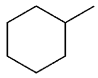
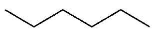
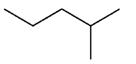
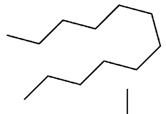
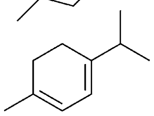
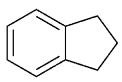
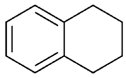
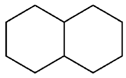
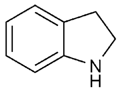
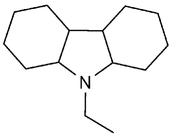


The reactivity of these substrates is primarily governed by the endothermicity of the corresponding alkane. The improved reactivity of cyclooctane is attributed to its lower enthalpy of dehydrogenation (23.3 kcal mol^{-1}), whereas this value is higher in the case of cyclohexane as the substrate (28.2 kcal mol^{-1}), which leads to lower catalyst activity.[15b] To our knowledge, the TONs and TOFs achieved in this study are, in most cases, significantly higher than previously reported values under such benign reaction conditions. The relationship between reactivity and endothermicity has been further established by a competition experiment in which *n*-octane and cyclooctane (1:1) were substrates. As expected, cyclooctane is more easily dehydrogenated (Table S3). In the case of cyclohexane and cyclooctane, the formation of traces (ca. 0.5 %) of dimeric side products (*m*/*z* 164 and *m*/*z* 220, respectively) was also observed.[16] Other linear alkanes such as hexane, 2-methylpentane, and dodecane achieved catalyst TONs of 462, 368, and 1100, respectively after 7 h. TONs of 1032 and 140 were obtained from the substrates α-terpenene and indane, respectively.

In general, the dehydrogenation of these *n*-alkanes produced the corresponding 2-alkenes preferentially. A control experiment with 1-octene as substrate gave, under identical reaction conditions, 28 % of isomerized 2-octene with traces of 3-octene after 5 h reaction time (Table S4). This result suggests that our rhodium-based photocatalytic method is also an efficient isomerization system.

In light of recent perspectives on shale gas,[4,5] the dehydrogenation capacity of one of the major shale gas com-

Table 3: Substrate scope of photocatalytic alkane dehydrogenation.[a]

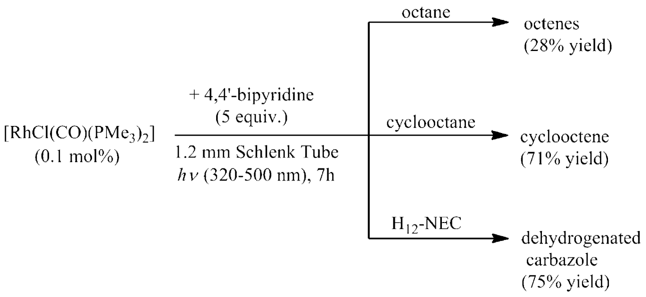
Entry	Alkane	Time [h]	TON	TOF[h^{-1}]
1[b]		7	1518	217
2[c]		7	2883	412
3[d]		7	975	139
4[e]		7	1200	171
5[f,g]		7	462	66
6[f,h]		7	368	53
7		7	1100	157
8		7	1032	148
9		7	140	20
10[i]		7	505	72
11[j]		7	357	51
12		7	154	24
13		7	708	101
14[k]		7	640	92

[a] Reaction conditions: $[Rh(PMe_3)_2(CO)Cl]$ catalyst (1.30 mg, 0.004 mmol), 4,4′-bipyridine (0.02 mmol), and the respective alkane (30 mmol) were placed in a Schlenk tube (wall thickness 1.2 mm). The reaction was carried out for the specified time under irradiation with light ($\lambda = 320$–500 nm) and constant stirring (1000 rpm) under a high stream of argon. The TON was determined by GC with respect to isooctane as an internal standard. [b] Product distribution: 1-octene (35 %), 2-octene (45 %; 35 % *trans* + 10 % *cis*), 3-octene (5 %), 4-octene (15 %), dienes (traces). [c] Traces of unidentified product with *m*/*z* 220 (as identified by GCMS). [d] Traces of unidentified product with *m*/*z* 164 (as identified by GCMS). [e] Product distribution: methylenecyclohexene (6 %), 1-methyl-1-cyclohexene (10 %), 1-methyl-3-cyclohexene (60 %), 1-methyl-4-cyclohexene (24 %). [f] Suffers alkane loss. [g] Product distribution: 1-hexene (5 %), 2-hexene (73 %), 3-hexene (22 %). [h] Product distribution: 4-methyl-1-pentene (72 %), 2-methyl-1-pentene (21 %), 4-methyl-2-pentene (5 %), 2-methyl-2-pentene (2 %). [i] Solvent: Perfluorodecalin. Determined by ^1H NMR spectroscopy with respect to mesitylene as an internal standard. Product distribution: 2-butene (> 99 %), 1-butene (traces). [j] Product distribution: 1,2-dihydronaphthalene (80 %), 1,4-dihydronaphthalene (> 19 %), naphthalene (traces). [k] Reaction conditions: $[Rh(PMe_3)_2(CO)Cl]$ catalyst (1.60 mg, 0.005 mmol), 4,4′-bipyridine (0.025 mmol). Product distribution: $H_{10}NEC$ (74 %), H_8NEC (20 %), remainder (6 %).

ponents, butane, was explored. To our delight, an excellent catalyst TON of up to 505 was observed after 7 h under the same photocatalytic reaction conditions. This result confirms the extensive applicability of our efficient photocatalytic method (Table 3; entry 10).

Recently, alkanes such as decalin, methylcyclohexane, indoline, and in particular, carbazole, have been proposed as liquid organic hydrogen carriers (LOHC) because of their high energy density, facile energy storage, and their ability to be safely transported.[17,18] Fully hydrogenated *N*-ethylcarbazole ($H_{12}NEC$), for example, has a theoretical hydrogen capacity of 5.8 % and caloric value of 1.9 $kWh\,kg^{-1}$.[18a] Excellent dehydrogenation of tetralin, decalin, indoline, and $H_{12}NEC$ was achieved after 7 h with catalyst TONs of 357, 154, 708, and 640, respectively (Table 3, entries 11–14). These dehydrogenations operate in essentially solvent-free conditions below 90 °C, which demonstrate the efficacy of the current photocatalytic procedure. It should be noted that the thermochemical dehydrogenation of $H_{12}NEC$ has previously been shown to require temperatures of more than 180 °C.[18]

In order to show the efficiency of the present photocatalytic method, selected reactions were performed using 3 mmol of substrate in the presence of 0.1 mol % of catalyst (Scheme 1). Excellent yields (71 % and 75 %, respectively) were obtained from cyclooctane and H_{12}-NEC as substrates. To our knowledge, such high yields have not been obtained in catalytic dehydrogenations without adding hydrogen acceptors. This is an important result for future practical applications. In the case of octane, slightly improved yields of octenes (28 % with similar product distribution) were observed due to the higher enthalpy of dehydrogenation. In the case of the dehydrogenation of $H_{12}NEC$, the reaction yielded H_8NEC as the major product.[19] The detection of H_8NEC as the major component after dehydrogenation is typical. Further dehydrogenation from H_8NEC is predicted to be difficult because of its weak absorption enthalpy on the planar pyrrole-type structure in the reverse process.[18b,c]



Scheme 1. Catalytic dehydrogenation reactions of alkanes in the presence of 0.1 mol % catalyst. Reaction conditions: $[RhCl(CO)(PMe_3)_2]$ (0.1 mol %) and 4,4′-bipy (5 equiv; 4,4′-bipy = 4,4′-bipyridine) in a Schlenk tube (wall width 1.2 mm), irradiating at $\lambda = 320$–500 nm for 7 h.

In conclusion, we have developed the most efficient acceptorless catalytic alkane dehydrogenation methodology known to date. By using light under optimal conditions, the well-known *trans*-$[Rh(PMe_3)_2(CO)Cl]$ complex provides high catalyst turnover numbers and excellent product yields. A variety of alkanes, including various liquid organic hydrogen carriers and shale gas components such as butane, can be efficiently dehydrogenated under environmentally benign conditions and at much lower temperatures than previously reported. Importantly, highly challenging alkane dehydrogenations can now be performed under more practical conditions, making the use of alkanes as olefin feedstock a real alternative for further synthetic manipulations. Further improvements towards the development of a second generation catalyst, with a focus on preventing the deactivation of the present catalyst, and detailed mechanistic studies are currently underway.

Experimental Section

General procedure: The specific glass vessel was initially charged with the $[Rh(PMe_3)_2(CO)Cl]$ catalyst (0.004 mmol) and the required additive (0.02 mmol), unless otherwise specified. The reaction vessel and water-cooled condenser were then evacuated completely under vacuum and backfilled with argon gas at least three times to ensure complete removal of residual air. The substrate (30 mmol), unless otherwise noted, was added to the vessel under an argon atmosphere. The glass vessel was then connected to a condenser under a strong flow of argon gas at the top of the condenser to remove evolved hydrogen. The vessel was covered by aluminum foil and irradiated with light from a Lumatec Superlite 400 source for a specified time. A high stirring rate (1000 rpm) was used to facilitate the removal of liberated hydrogen. After the reaction, the vessel was cooled to room temperature. The product yield/turnover number (TON) was then determined by GC or NMR spectroscopy with respect to isooctane or mesitylene, respectively, as internal standard. Turnover numbers represented in tables are expressed as [mmol of product]/[mmol of catalyst] and TOF (turn over frequency) is expressed as (TON/time in h). A more detailed experimental procedure is provided in the Supporting Information.

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[19] a) Product distribution from *n*-octane: 1-octene (34 %), 2-octene (45 %; 33 % *trans* + 12 % *cis*), 3-octene (6 %), 4-octene (15 %), dienes (traces); b) product distribution from H_{12}NEC: H_8NEC (70 %), NEC (23 %), remainder (7 %).

Communications

Photocatalysis

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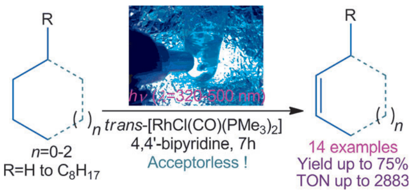
M. Beller* ________ ■■■■–■■■■

Towards a Practical Development of Light-Driven Acceptorless Alkane Dehydrogenation



Blue (light) is green: The efficient light-induced atom-economical alkane dehydrogenation of various linear and cyclic alkanes (including shale gas constituents and liquid organic hydrogen carriers) was accomplished using *trans*-[Rh(PMe_3)$_2$(CO)Cl] as catalyst in the presence of a specific nitrogenous additive. It provides a benign alternative to the direct use of alkanes as olefin feedstocks.