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Palladium/Carbon Catalyzed Hydrogen Transfer Reactions using Magnesium/Water as Hydrogen Donor

**Omari Muhammad · Sachin U. Sonavane ·
Yoel Sasson · Mandan Chidambaram**

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Abstract A new methodology is developed for the hydrogenation reaction using magnesium/water system, as hydrogen source under catalytic palladium on activated carbon (Pd/C). The method is highly efficient for the chemoselective reduction of wide range of unsaturated aldehydes and ketones. The process is also found to be suitable when we think about green chemistry for the eco-friendly hydro-dehalogenation of aromatics. From practical point of view this new methodology is the most attractive, efficient, economical and convenient approach towards industrially important reduction transformations. This report is intended to highlight the use of Mg/H_2O system in these organic transformations which can be easily adopted in industrial scale for the bulk production of hydrogenation products.

Keywords Palladium/Carbon · Magnesium/Water · Hydrogenation · Hydro-dehalogenation · Deutero-dehalogenation

1 Introduction

In recent years, green chemistry has received increased attention. The general areas of investigation in green chemistry include selections of feedstock's, reagents, solvents, reaction conditions, catalysts and the design of safer chemicals for safe and cheap practical methodologies. On the other hand, alternative reagents are also the focus of attention in green chemistry circle. The efficient catalytic reduction of water for generation of hydrogen is one of the most challenging transformations in chemistry [1]. Water is the ultimate hydrogen source, being both safe and plentiful. Recently few researchers reported the hydrogenation using H_2O or D_2O as a hydrogen source [2]. Hydrogen gas, in addition to its potential as an eco-friendly energy carrier, is one of the fundamental feed stocks in the contemporary chemical industries [3].

It has been long known that magnesium in methanol or in ethyl or isopropyl alcohol can be used for the reduction of various functional groups [4]. Utility of Mg/MeOH as an electron transfer reagent has appeared in literature rather sporadically since the ability of Mg/MeOH to reduce functional groups such as nitro, oxime, ketone and halogen was first discovered by Zechmeister [5].

$$Mg + 2MeOH \longrightarrow Mg(OMe)_2 + H_2$$

There after its use has been expanded not only to the selective reduction of various functional groups, but also to the reduction of conjugated double and triple bonds tethered to diverse functional groups such as esters [6], nitriles [7], amides [8] and aromatics [9] to the corresponding saturated analogs. Mg/MeOH has been demonstrated as a convenient single electron transfer reagent for a number of reductive reactions [10].

From environmental point of view, Mg/H_2O is preferred methodology that can supersede the well-known limitations of catalytic hydrogenation using molecular hydrogen and high pressure vessels. As water is a universal solvent,

O. Muhammad · S. U. Sonavane · Y. Sasson ·
M. Chidambaram (✉)
Casali Institute of Applied Chemistry, Hebrew University
of Jerusalem, Jerusalem 91904, Israel
e-mail: mandan.chidambaram@berkeley.edu

Present Address:
M. Chidambaram
Energy Biosciences Institute, University of California at
Berkeley, 350 Calvin Hall, Berkeley, CA 94720-2321, USA

this system is advantageous over Mg/MeOH too. The reaction of magnesium with water is extremely important and very useful in chemical applications, for example, to generate heat or dihydrogen. With magnesium so widespread, the magnesium-water reaction should have been intensively studied, but the reaction is poorly described, except to emphasize its slowness [11]. The sluggishness of the magnesium-water reaction, despite its favorable free energy change is due to passivation of the metal by an unreactive oxide/hydroxide layer on the surface [12].

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Anions presumed to be unreactive, particularly chloride, are often added as catalysts to speed up the reaction [13], because they destroy the oxide/hydroxide layer's integrity. Even this anionic catalysis of the reaction is often insufficient for practical use, so it is further accelerated by using the metal milled with a small amount of Fe [14]. Previous researchers demonstrated the production of di-hydrogen using magnesium-water system and its application for the scavenging studies but ignored its utilization for the practically important organic transformation. We believe that the yield of dihydrogen can be utilized well to reduce complex organic molecules. Its merit should be emphasized in its economy, safety, versatility, environmental benignancy and handling, compared to its equivalent metal reagent [15]. In our laboratory previously we have studied coupling of haloaryls to biaryls [16] and reduction of aldehydes to alcohols [17] using Zn/H_2O system.

Here we report the safe hydrogen generation source using magnesium-water reaction and its wider technological application for the industrially important hydrogenation and hydro-dehalogenation reactions using catalytic Pd/C. We have observed that, under remarkably mild conditions, the heterogeneous reaction of water with plain magnesium powder to magnesium hydroxide and hydrogen gas. Water reduction experiments in the presence of organic hydrogen acceptors are reported, with a different reaction pathway, involving direct hydrogen transfer from water to the organic substrate. Based on the observation using current system and earlier studies over Zn/H_2O system in our lab we also propose a modified mechanism for hydrogen generation and subsequently hydrogenation reactions.

2 Experimental Section

2.1 Direct Hydrogen Transfer Reactions

In a typical reaction, 4-phenyl-3-buten-2-one (10 mmol), magnesium (10 mmol), water (15 mL), catalytic amount of $NiCl_2$ (1 mmol) and 5% Pd/C (0.5 mol% of substrate) was charged to a batch reactor. After stirring for an appropriate reaction period at 70 C, after which quantitative conversion to 4-phenyl-butane-2-one was measured. Depending on reaction conditions saturated carbonyl was found to be the product of the reaction system. Good to moderate yields were obtained using various unsaturated substrates. Purity of the products was confirmed by GC and GC-MS.

2.2 Hydro-Dehalogenation of Haloarenes

In an archetypal reaction, 4-bromoanisole (10 mmol), magnesium (10 mmol), water (15 mL), catalytic amount of $NiCl_2$ (1 mmol) and 5% Pd/C (0.5 mol% of substrate) was charged to a batch reactor. After stirring for an appropriate reaction period at 70 C, after which quantitative conversion to anisole was found to be the product of the reaction system. Good to moderate yields were obtained using various haloarenes as a substrates this clears the usefulness of system for the environmentally benign hydro-dehalogenation. Purity of the products was confirmed by GC and GC-MS.

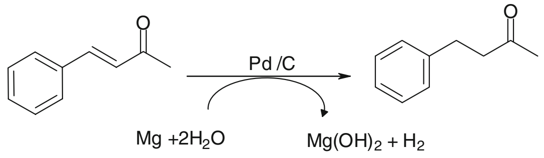
2.3 Deuteration of Haloarenes

In a representative reaction, 4-Iodoanisole (10 mmol), magnesium (10 mmol), D_2O (15 mL), catalytic amount of $NiCl_2$ (1 mmol) and 5% Pd/C (0.5 mol% of substrate) was charged to a batch reactor. After stirring for an appropriate reaction period at 70 C, filtration, followed by extraction with ethyl acetate and distillation afford deuteriated anisole as a product of the reaction system. Purity of the products was confirmed by GC and GC-MS, Deuteriated anisole GC-MS *m/z* 109 (*cf.* for anisole *m/z* 108).

In all the cases, after completion of the reaction, the product was extracted with two consecutive portions of ethyl acetate; the combined organic layers were washed well with water and dried over sodium sulfate. The organic layer was concentrated under reduced pressure to afford a product. Pure products were obtained by purification on a short silica gel column. All the products had satisfactory ^1H NMR, IR data and were compared with authentic samples.

3 Results and Discussion

Hydrogenation of benzalacetone (4-phenyl-3-buten-2-one) to benzylacetone (4-phenyl-2-butanone) was chosen as a model reaction in the present method of magnesium–water using 5% Pd/C as catalyst (Scheme 1). Two separate reactions with 10 mmol of 4-phenyl-3-buten-2-one, 10 mmol of magnesium, 15 mL of water, catalytic amount of $NiCl_2$ and 5% Pd/C was stirred for an appropriate reaction period at 25 and 70 C, respectively and quantitative conversion to 4-phenyl-2-butanone was measured using GC



Scheme 1 Generation and utilization of hydrogen in the hydrogenation of 4-phenyl-3-butene-2-one to 4-phenyl-2-butanone

with capillary column. When the temperature of the reaction was increased from 25 C to 70 C, the yield to saturated carbonyl was increased from 35% to 93%, hence the reaction temperature was kept as 70 C in all the experiments.

The influence of various reaction parameters on the production of hydrogen and its utilization in in-situ hydrogenation of 4-phenyl-3-buten-2-one is shown in Table 1 with respect to conversion of substrate. The effect of amount of magnesium was studied using 5, 10 and 15 mmol (Entries 1–3) of magnesium. The conversion obtained using 5 mmol of magnesium showed that there was no sufficient production of hydrogen, which is further proved by using 10 mmol of magnesium where 100% conversion and 93% yield were obtained. Further increase of magnesium (15 mmol) showed less conversion which is because of the deactivation of magnesium particles by the large formation of $Mg(OH)_2$, a solid agglomeration. This phenomenon is further confirmed by using different particle sizes of magnesium (Entries 4–6). The average particle size of 0.1 to 0.5 μm gave 100% conversion, whereas big particle size (0.5 to 1.5 μm) showed only 75% conversion because of the poor reaction between magnesium and water and the formation of big aggregates of $Mg(OH)_2$, which hinders the contact between magnesium and water.

The effect of Cl^- ion was studied with and without NaCl. Without NaCl poor conversion was obtained whereas with NaCl 100% conversion with 93% yield was obtained (Entries 7–8). We believe that during reaction of magnesium with water forms $Mg(OH)_2$ which hindered the reaction between water and magnesium to generate hydrogen further. Chloride ion readily replaces hydroxide ion, where it reacts with $Mg(OH)_2$, for example, forming the more soluble Mg(OH)Cl or $MgCl_2$, thereby causing channels in the precipitate and in the oxide/hydroxide layer through which water can reach the magnesium and thus production of hydrogen continued.

Table 1 Hydrogenation of 4-phenyl-3-buten-2-one to 4-phenyl-2-butanone under various reaction parameters[a]

Entry	Parameters	Conversion (%)
Mg (mmol)		
1	5.0	60
2	10.0	100
3	15.0	92
Mg particle (μm)		
4	0.08–0.1	50
5	0.1–0.5	100
6	0.5–1.5	75
Effect of Cl−		
7	Without NaCl	55
8	With NaCl	100
Metal addition effect		
9	Pd	45
10	Fe	75
11	Ni	100
Effect of MCl_2 (1 mmol)		
12	$FeCl_3$	80
13	$ZnCl_2$	75
14	$NiCl_2$	100
Pd/C (mol%)		
15	None	0
16	0.05	80
17	0.5	100
18	1.0	100

[a] Standard reaction conditions: substrate 10 mmol; Mg, 10 mmol; 5% Pd/C, 0.5 mol% of substrate; $MCl_{2,}$ 1 mmol; stir for appropriate time at 70 C; 15 mL total reaction volume (water). Conversion is based on GC area, corrected by the presence of an internal standard. In all the cases very high yield of product (>90%) was obtained

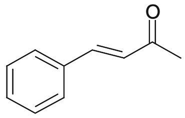
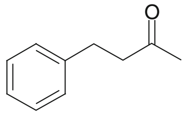
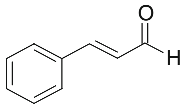
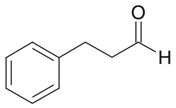
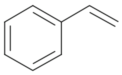
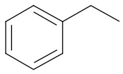
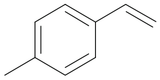
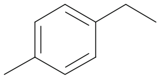
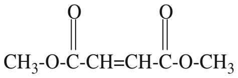
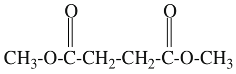
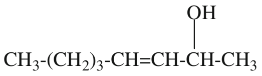
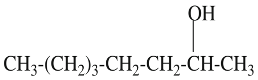
Taub et al. [14] mentioned that trace or catalytic amount of metal increases hydrogen generation in magnesium water reaction where a small amount of metal (Iron) along with NaCl enhances the production of hydrogen. Authors noted that the metal acted as activator and the chloride from NaCl acted as catalyst for the enhancement of hydrogen production using magnesium/water. To utilize the same advantage in our system we studied different metals in catalytic amount (Entries 9–11) with NaCl and found that a small amount of nickel accelerates the product formation. This acceleration may not be due to catalysis, since a very small amount of Ni is utilized in the reaction but extent of interfacial contact between Mg and Ni plays important role. When we were confident about the effect of catalytic amount of nickel and chloride ion, we carried out new experiments where we used metal halides. We have studied effect of various MCl_2 where M = Fe, Ni, Zn (Entries 12–14) towards the reduction product and we reached the conclusion that $NiCl_2$ can be used in the present system instead separate use of NaCl and Ni particles. Moreover, the phenomenological rate of dihydrogen formation will depend on the total availability of unreacted magnesium sites, which will generally increases with increasing surface area. We believe that reaction between Mg and water form $Mg(OH)_2$ which rises the pH to about 11. With the addition of acidic $NiCl_2$, the mixture hydrolyzed extensively hence lowering the pH to 2 so that the precipitate does not form and the oxide/hydroxide layer is rapidly removed, hence the magnesium surface is readily available for further reaction. We assume that $NiCl_2$ does not alter the chemical nature of the intermediates, but rather, that it modifies the physical microenvironment of the catalyst, facilitate the approach of the organic substrate. In depth study of role of nickel chloride will be carried out using the methodology presented by Gaikwad et al. [18] and reported separately.

In the absence of Pd/C catalyst, there was no product formation, whereas with 0.5 mol% of catalyst loading showed complete 100% conversion (Entries 15–18). Further, presence of 0.05 mol% catalyst in the reaction system showed 80% conversion. This clearly says that there was insufficiency in the catalyst amount for the completion of reaction. The unlikely possibility of hydrogen being generated via a reaction between Pd/C and water can also be ruled out in the light of the failure to hydrogenate in the control experiment made in the absence of magnesium, since the reaction between Pd^0 and water is thermodynamically unfavorable.

To further explore the utility of the present system several alkenes and α,*β*-unsaturated carbonyl compounds over magnesium-water system using Pd/C catalyst were reduced. Table 2 summarizes the results, wherein the substrates were reduced products in excellent manner. The system reduces olefinic bonds, keeping intact the carbonyl groups. The selective reduction can be explained on the basis of the actual active species involved in the reduction process, which strongly depends on the reaction conditions. Thus, when Pd/C is used in combination with in-situ hydrogen generation from magnesium/water system, selective reduction of the olefinic bond produces saturated carbonyl compounds.

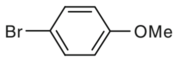
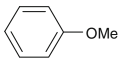
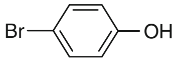
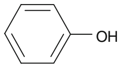
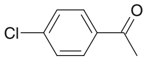
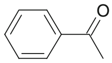
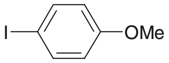
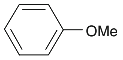
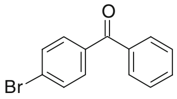
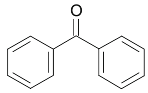
Table 3 summarizes the results of hydro-dehalogenation of aryl halides using this methodology. The hydro-dehalogenation of –Cl–Br and –I functions were achieved in good yields. Functional groups such as $-COCH_3$, –CO–, –OH and $-OCH_3$ were tolerated. Furthermore, in practical point of view hydrogen generation and its application is more effective than several other catalytic systems, which require much longer reaction times, typically 1–2 days, to achieve good yields [19]. The conversion was much faster

Table 2 Hydrogenation of unsaturated compounds using magnesium/water system[a]

Entry	Reactants	Products	T (h)	Conversion (%)
1			5.5	100
2			4.5	100
3			5.0	97
4			4.0	100
5	 $CH_3\text{-O-}\overset{\overset{O}{\Vert}}{C}\text{-CH=CH-}\overset{\overset{O}{\Vert}}{C}\text{-O-}CH_3$	 $CH_3\text{-O-}\overset{\overset{O}{\Vert}}{C}\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{O}{\Vert}}{C}\text{-O-}CH_3$	6.0	90
6	$CH_3\text{–CH=CH–CHO}$	$CH_3\text{–}CH_2\text{–}CH_2\text{–CHO}$	5.5	98
7	 $CH_3\text{-}(CH_2)_3\text{-CH=CH-}\overset{\overset{OH}{\vert}}{CH}\text{-}CH_3$	 $CH_3\text{-}(CH_2)_3\text{-}CH_2\text{-}CH_2\text{-}\overset{\overset{OH}{\vert}}{CH}\text{-}CH_3$	6.0	90

[a] Reaction conditions: substrate 10 mmol; Mg, 10 mmol; 5% Pd/C, 0.5 mol% of substrate; $NiCl_2$, 1 mmol; stir for appropriate time at 70 C; 15 mL total reaction volume (water). Conversion is based on GC area, corrected by the presence of an internal standard. In all the cases very high yield of product (>90%) was obtained by GC

Table 3 Hydro-dehalogenation of aryl halides using magnesium water system[a]

Entry	Reactants	Products	T (h)	Conversion (%)
1			5.0	90
2			4.5	95
3			6.0	85
4			5.0	90
5			5.0	80

[a] Reaction conditions: substrate 10 mmol; Mg, 10 mmol; 5% Pd/C, 0.5 mol% of substrate; $NiCl_2$, 1 mmol; stir for appropriate time at 70 C; 15 mL total reaction volume (water). Conversion is based on GC area, corrected by the presence of an internal standard. In all the cases high yield of product (>80%) was obtained by GC

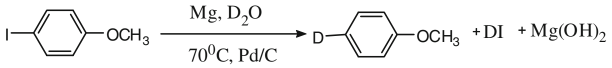
and cleaner than conventional methods and moreover, in the present case, the reaction occurs under mild reaction conditions. Thus, the present hydrogen generation methodology is a highly selective route for environmentally benign organic transformations. In particular, the role of water as the hydrogen source and catalyst regenerator becomes apparent.

We also studied the application of said method in deuteration of aryls at specific sites on the aromatic ring. This was simply achieved by reductive deutero-dehalogenation of haloaromatics using D_2O as deuteration agent [17]. As shown in scheme 2, for example, deuteroanisole was isolated in 72% yield, from corresponding 4-Iodoanisole (85% conversion) after 4 h of reaction time.

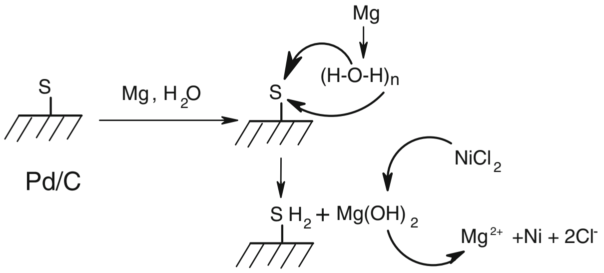
Here we propose a possible mechanism (modified from our earlier proposed mechanism of hydrogen production from Zn/H_2O [17]) for this unique transformation where hydrogen-transfer takes place from 'magnesium activated' water to the substrate, rather than a dehydrogenation–hydrogenation (Scheme 3) sequence involving molecular hydrogen.

This is supported by the following reasons

i. The normal condition experiment could be carried out in an open vessel, and no free hydrogen gas was detected in the presence of substrate.



Scheme 2 Deutero-dehalogenation of 4-Iodoanisole



Scheme 3 Proposed mechanism for hydrogen transfer from magnesium activated water to an organic substrate S

ii. Experiments in open and closed vessel evidenced similar reactivity. In the presence of organic hydrogen acceptor (S); the possible pathway will be the direct hydrogen transfer from water to the adsorbed substrate, with no Pd-H species.

4 Conclusions

In conclusion water molecules that are activated by magnesium particles can decompose catalytically to hydrogen and magnesium hydroxide. Possibly, in the presence of organic hydrogen acceptors, direct hydrogen transfer from water to the organic substrate is realized with the help of Pd/C. Thus, Mg/H_2O is a reagent of choice for versatile organic reactions. It is simple to use, safe to handle and an environmentally benign reagent compared to other methods such as catalytic hydrogenation using molecular hydrogen and even with Mg/MeOH.

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References

1. Bolton JR (1996) Sol Energy 57:37; Amouyal E (1995) Sol Energy Mater Sol Cells 38:249; Tamaura Y, Steinfeld A, Kuhn P, Ehrensberger K (1995) Energy 20:325; Weirich W, Biallas B, Kungler B, Oertel M, Pietsch M, Winkelmann U (1986) Int J Hydrogen Energ 11:459
2. Takashi S, Watanabe S, Kiuchi H, Oi S, Inoue Y (2006) Tetrahedron Lett 47:7703; Shirakawa E, Otsuka H, Hayashi T (2005) Chem Commun 5885
3. Weissermel K, Arpe H-J (1993) Ind Org Chem, 2nd edn. VCH, Weinheim, p 23
4. Profitt JA, Watt DS, Corey EJ (1975) J Org Chem 40:127
5. Zechmeister L, Rom P (1929) Justus Liebigs Ann Chem 117:486
6. Walkup RD, Park GS (1990) J Am Chem Soc 112:1597
7. Corey EJ, Watt DS (1973) J Am Chem Soc 95:2303; Lansbury PT, Galbo JP, Springer JP (1988) Tetrahedron Lett 29:147; Paquette LA, Okazaki ME, Caille JC (1988) J Org Chem 53:477
8. Brettle R, Shibib SM (1980) Tetrahedron Lett 21:2915; Brettle R, Shibib SM (1981) J Chem Soc Perkin Trans I 2912; Danieli B, Palmisano G, Lesma G, Riva R, Riva S, Demartin F, Masciocchi N (1984) J Org Chem 49:4138; Ainscow RB, Brettle R, Shibib SM (1985) J Chem Soc Perkin Trans I:1781
9. Hutchins RO, Zipkin RE, Taffer IM, Sivakumar R, Monaghan A, Elisseou EM (1989) Tetrahedron Lett 30:55
10. Lee GH, Choi EB, Lee E, Pak CS (1995) Tetrahedron Lett 36:5607
11. Topper HH (1978) Edu Chem 15:134
12. Perrault GG (1978) Encyclopedia of electrochemistry of the elements. In: Bard AJ (ed) Marcel Dekker, New York and Basel, vol. VIII, 263pp
13. Folomeev AI (1986) Zh Prikl Khim 59:267
14. Taub IA, Roberts W, LaGambina S, Kustin K (2002) J Phys Chem A 106:8070
15. Pasupathy K (2003) Synlett 12:1942
16. Mukhopadhyay S, Rothenberg G, Gitis D, Sasson Y (2000) Org Lett 2:211
17. Mukhopadhyay S, Rothenberg G, Wiener H, Sasson Y (2000) New J Chem 24:305
18. Gaikwad AV, Holuigue A, Thathagar MB, ten Elshof JE, Rothenberg G (2007) Chem Euro J 13:6908
19. Adimurthy S, Ramachandraiah G, Bedekar AV (2003) Tetrahedron Lett 44:6391; Cellier PA, Spindler JF, Taillefer M, Cristau HJ (2003) Tetrahedron Lett 44:7191