Solid–solid palladium-catalysed water reduction with zinc: mechanisms of hydrogen generation and direct hydrogen transfer reactions†

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Received (in Montpellier, France) 23rd February 2000, Accepted 1st March 2000
Published on the Web 12th April 2000

Facile generation of hydrogen gas from water takes place under moderate conditions in the presence of zinc powder and catalytic palladium on carbon; 82% conversion of zinc is obtained. An unusually large kinetic isotope effect is observed using D_2O ($k_H/k_D = 14$), which may reflect the cleavage of both O–H bonds in the rate-determining step. Experiments using D_2O–H_2O mixtures evidence that water molecules adsorbed on the catalyst surface undergo H–D exchange reactions (with molecules from the solvent bulk) that are approximately 100 times faster than the hydrogen generation reaction. The primary factors in this system appear to be palladium–hydrogen and zinc–oxygen interactions. Conversely, in the presence of an organic hydrogen acceptor, such as benzaldehyde, a different course is realised, consisting of direct hydrogen transfer from "zinc-activated" water to the substrate, without the participation of Pd–H intermediates. Quantitative hydrogenation of benzaldehyde to benzyl alcohol, and of aromatic nitro compounds to the corresponding amines, is obtained. Another application of the above system is the specific deutero-dehalogenation of aromatic halides. Possible mechanisms and the implications of a chemical reaction involving two macroscopic solid particles are discussed.

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. Hydrogen gas, in addition to its potential as an eco-friendly energy resource, is one of the fundamental feed stocks in the contemporary chemical industry.[2]

The reduction reaction of water with zinc is known to occur at extreme temperatures and pressures. Thus, ZnO and H_2 have been detected under supercritical conditions[3] at 450 °C, or at 250–325 °C at 221 bar pressure.[4] It has also been reported that electrochemical coating of zinc particles with noble metals (*e.g.*, Rh, Pt, Pd)[5a] or with Ni[5b] can facilitate the reaction between zinc and water at the particle interface. A comparable concept has also been patented for maintaining a dry atmosphere within electronic devices.[6] Although the above techniques require special apparatus, and were only performed on a small scale, they demonstrate the thermodynamic feasibility of the reaction of water and zinc, provided that the activation energy barrier can be negotiated.§

We have now observed that palladium on carbon catalyses, under remarkably mild conditions, the heterogeneous reaction of water with plain zinc powder to zinc oxide and hydrogen gas. In this paper, this chemical process is studied through the examination of rate profiles and kinetic isotope effects. A reaction mechanism is proposed and the implications of a chemical reaction at the microscopic interface between two macroscopic metallic particles are discussed. Water reduction experiments in the presence of organic hydrogen acceptors are also reported, wherein a different reaction pathway, involving direct hydrogen transfer from water to the organic substrate, is evidenced. The roles of Pd–H species as intermediates in the organic and in the inorganic systems are discussed. The application of this process to *in situ* site-specific deuteration of aromatic molecules is also described.

Results

Hydrogen generation from water reduction

In a typical experiment [eqn. (1)], 1 equiv. of untreated zinc powder (40 mesh size) was mixed in an autoclave with an excess¶ of water and 0.005 equiv. of 5% Pd/C. At 120 °C, the reaction ceased when 82% of the zinc had been consumed (34 atm H_2 pressure), probably due to coating of the zinc particles with ZnO (*vide infra*). A 100% mass balance was evidenced by gravimetric analysis of zinc oxide. Analysis of the reaction profile showed that the reaction follows a first-order rate equation up to 60% conversion of zinc. Hydrogen generation was found to be equally facile under both neutral and basic conditions ($6.6 < \mathrm{pH} < 12.8$). Control reactions (25–120 °C) confirmed that no hydrogen was generated in the absence of the catalyst, nor was hydrogen detected when palladium on carbon was stirred with water in the absence of zinc. Furthermore, blank experiments using glass vessels and Teflon propellers gave similar results to those using stainless steel equipment, indicating that the steel apparatus plays no part in the reaction.

$$\mathrm{Zn_{(s)}} + \mathrm{H_2O_{(l)}} \xrightarrow[\text{35–120 °C, 10–300 min}]{\text{0.4–1 mol \% of 5\% Pd/C}} \mathrm{ZnO_{(s)}} + \mathrm{H_{2(g)}} \qquad (1)$$

As mentioned above, hydrogen generation stopped after *ca.* 82% zinc conversion. This does not reflect catalyst deactivation, as the reaction did not resume when fresh portions of Pd/C were added. Conversely, when fresh zinc powder was added, hydrogen generation resumed. The deactivation became more pronounced when larger zinc particles were

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† *Non-SI units employed*: 1 bar = 10^5 Pa; 1 atm = 101.3 kPa; 1 psi = 6.9×10^3 Pa; 1 kcal ≈ 4.2 kJ.

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DOI: 10.1039/b001655l

employed, such that with 1 mm diameter particles the reaction stopped after less than 15% of the zinc had been consumed.

Deuterium isotope effect studies

When the reaction was performed with D_2O instead of H_2O, an uncommonly large kinetic isotope effect[8a] was measured (Fig. 1, $k_{H_2O}/k_{D_2O} = 14.2$), indicating the participation of O–H (or O–D) bond scission in the rate-determining step. This unusual magnitude[8b] of the isotope effect may be attributed to two O–H bonds being broken simultaneously in the rate-determining step.

Remarkably, an equimolar mixture‖ (Mix1, Fig. 2) of D_2O and H_2O, for which a value of $k_{H_2O}/k_{Mix1} \approx 7$ could be intuitively expected, actually displayed the same activity as pure H_2O (*i.e.*, $k_{H_2O} = k_{Mix1}$). This observation may be explained by taking into account fast O–H and O–D exchange reactions, which can occur not only in solution but also (and apparently much faster) when the molecule is activated on the catalyst surface (*cf.* aqueous formate salts and Pd/C[10]). In the case of Mix1, when a D_2O molecule is adsorbed on the palladium catalyst, it is activated and may freely exchange its D atoms for H atoms with an H_2O molecule from the bulk of the solvent. Of course, the effects of this fast reaction would not be observable in pure H_2O or D_2O. However, in a mixture such as Mix1, D_2O molecules would be apt to exchange their D atoms for H atoms and H_2 gas would be released more often than HD or D_2. As these kinetic studies are based on the measurements of *initial rates*, Mix1, which contains about 25 mol% of H_2O, would display the same behaviour as pure H_2O.

In order to try and assess the relative rates of the H–D exchange and the water reduction reactions, we performed another experiment using a 98 : 2 molar ratio mixture of D_2O : H_2O (Mix2). As shown in Fig. 2, the pressure initially rises with a rate corresponding to that of pure H_2O reduction ($k_{1,Mix2} \approx k_{H_2O}$), and then levels out with a rate corresponding tothat of pure D_2O reduction ($k_{2,Mix2} \approx k_{D_2O}$). This sets the rate constant for the H–D exchange reaction at about two orders of magnitude higher than the catalytic reduction of D_2O on the palladium surface.

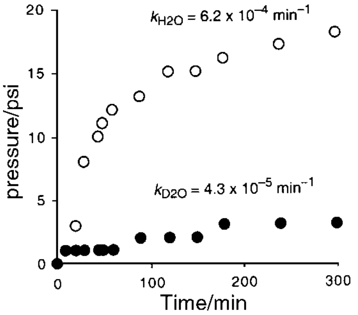


Fig. 1 Pressure generated in the presence of (○) H_2O and (●) D_2O. Reaction conditions: 150 mmol Zn, 300 mmol H_2O or D_2O, 1 mol% Pd (5% Pd/C), 75 °C, 100 ml dry PhMe.

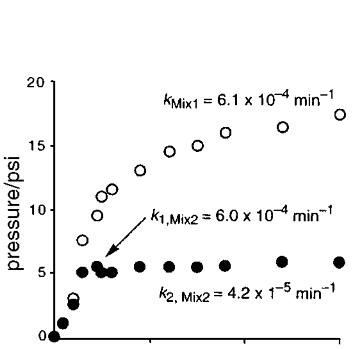
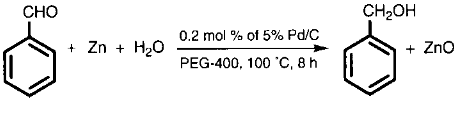


Fig. 2 Pressure generated in the presence of (○) Mix1 and (●) Mix2. Reaction conditions: 150 mmol Zn, 300 mmol Mix1 or Mix2, 1 mol% Pd (5% Pd/C), 75 °C, 100 ml dry PhMe.

Water, of course, could not be used as diluent in the above isotope effect studies. Dry PhMe was therefore used, after blank reactions showed that its presence does not affect the reaction.

Using water as a direct hydrogen donor

The zinc–water system was also found to affect direct hydrogen transfer reactions from water to organic substrates. For example, benzaldehyde was quantitatively reduced to benzyl alcohol [eqn. (2)]. Excellent (>99%) yields were similarly obtained in the reductions of nitrobenzene to aniline, and of 4-nitroanisole to 4-aminoanisole.



(2)

We believe that this reaction is a true hydrogen-transfer process from "zinc-activated" water to the substrate, rather than a dehydrogenation-hydrogenation sequence involving molecular hydrogen. This is supported by the following findings: (*i*) experiments in open and closed vessels evidenced similar hydrogenation rates; (*ii*) no free hydrogen was released from the system; (*iii*) the reduction of benzaldehyde with D_2O to benzyl-*d*-alcohol-*d* showed only a low isotope effect ($k_H/k_D = 1.4$);** and (*iv*) initial H_2 production rates (without an organic substrate) were slower than the initial rates (up to 20% conversion) of reduction in the presence of an organic substrate, the ratio $k_{reduction} : k_{H_2\ generation}$ being approximately 2 : 1.

Another interesting application for the method outlined above is the deuteration of aryls at specific sites on the aromatic ring. This can be done simply by reductive deuterodehalogenation of haloaromatics. As shown in eqn. (3), for example, 1-deuterobenzene, C_6H_5D, was isolated in 56% yield from bromobenzene (72% conversion), the only other product being biphenyl.

$$C_6H_5Br + Zn + D_2O \xrightarrow[100\,^{\circ}C,\ 8\ h]{0.5\ mol\ \%\ Pd/C} C_6H_5D + DBr + ZnO \qquad (3)$$

Discussion

Since Pd^0 does not react with water in the absence of zinc, it is unlikely that palladium oxide is an intermediate in our system.†† Rather, it appears that zinc acts as an oxygen acceptor, while palladium interacts only with the hydrogen atoms. The sensitivity of the reaction to the zinc surface area, plus the fact that the deactivation is dependent on zinc, rather than on palladium, all point to zinc–oxygen and palladium–hydrogen interactions.

Based on the experimental results, we may envisage two possible mechanistic options for this remarkable transformation. The first, and more probable, is that the reaction occurs at the interface between two macroscopic particles (see Fig. 3). In this model, water first adsorbs on the palladium surface, whereby the O–H bonds are activated (see Fig. 4). Following this, zinc donates two electrons to the oxygen atom and both O–H bonds are cleaved simultaneously in the rate-determining step. The two $H^{\cdot}$ radicals interact with Pd^0 to form palladium hydrides, and then, by reductive elimination, H_2 leaves the palladium surface.

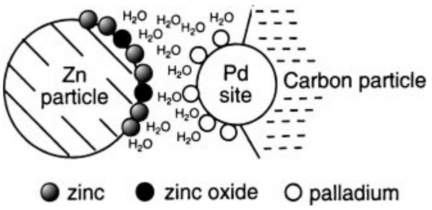


Fig. 3 Cartoon of the solid–solid water reduction reaction.

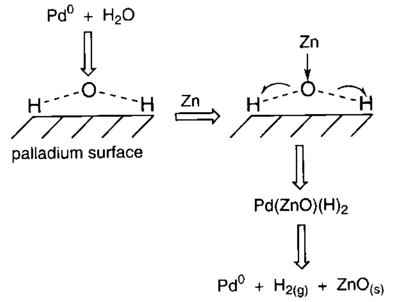


Fig. 4 Suggested mechanism for hydrogen formation.

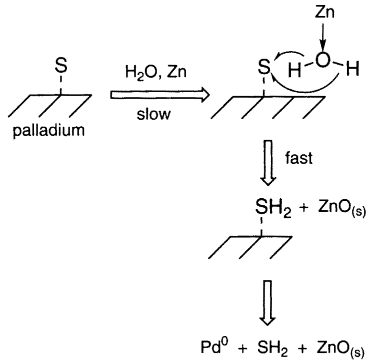


Fig. 5 Suggested mechanism for hydrogen transfer from "zinc-activated" water to an organic substrate S.

A second possible option is that a classical electrochemical mechanism occurs *via* direct contact between the solid particles. However, inasmuch as any chemical reaction is an "electrochemical reaction", it should be noted that zinc, zinc oxide and Pd/C are all insoluble in water under the reaction conditions. The isotopic effects observed, plus the fact that the reaction contains no electrolyte, make a classical electrochemical mechanism unlikely in this case.

In the presence of an organic hydrogen acceptor (S), the experimental results point to a different reaction route. This pathway (Fig. 5) consists of direct hydrogen transfer from water to the adsorbed substrate, with no Pd–H species. *The latter cannot participate as intermediates, since their formation is rate-determining in the slower hydrogen generation process.* Accordingly, the rate-determining step may now be the adsorption of water to a free active site. Indeed, it has been shown in similar cases that the adsorption of the H-donor (in this case, water) is rate determining.[11] Furthermore, the presence of the organic substrate S and/or of its product SH_2 alters the system, so that the deactivation of the zinc particles described above is evidently prevented (quantitative hydrogenation of S to SH_2 takes place when using molar equivalents of zinc and S).

Conclusion

Water molecules that are activated by zinc particles can decompose catalytically to hydrogen and zinc oxide in the presence of Pd/C. Possibly, this reaction occurs at the interface between two macroscopic solids. In the presence of organic hydrogen acceptors, direct hydrogen transfer from water to the organic substrate is realised.

Experimental

General

GC and GC-MS analyses were performed using an HP-5890 gas chromatograph with a 50% diphenyl–50% dimethylpolysiloxane packed column (25 m/0.53 mm). Chemicals were purchased from commercial firms (>98% pure) and used without further purification. Satisfactory spectral analyses were obtained for all products. Reactions were performed in a 300 ml stainless steel Parr autoclave equipped with a six-bladed propeller, an external heating mantle and a gas cooling system.

Procedures

Water reduction reaction. Zn powder (40 mesh size, 15.0 g, 230 mmol) was mixed in an autoclave with 2.0 g 5% Pd/C (0.9 mmol Pd) and 125 ml H_2O at 75 °C. An 82% conversion of zinc was achieved after 72 h, with a pressure of 34 atm H_2.

Direct hydrogen transfer reactions. As an example, using the hydrogen transfer from water to benzaldehyde reaction: 5.0 g of benzaldehyde (47 mmol), 3.3 g (52 mmol) Zn powder, 0.2 g 5% Pd/C (0.09 mmol Pd), 1 g PEG-400, and 45 ml H_2O were mixed at 100 °C for 8 h, after which quantitative conversion to benzyl alcohol was measured. Hydrogenations of nitrobenzene (44 mmol, 12 h, 1.2 mol% Pd, >99% yield to aniline) and of 4-methoxynitrobenzene (44 mmol, 14 h, 1.2 mol% Pd, 100% yield to 4-methoxyaniline) were similarly performed.

Deuteration of halobenzenes. For C_6H_5D from C_6H_5Br: 5.0 g C_6H_5Br (32 mmol), 4.2 g (64 mmol) Zn powder, 0.35 g 5% Pd/C (0.16 mmol Pd), and 25 ml D_2O were mixed at 100 °C for 18 h (72% conversion of bromobenzene). Filtration, followed by extraction with 25 ml CH_2Cl_2 and distillation afforded 1.0 g (56% isolated yield based on starting material) of 1-deuterobenzene, C_6H_5D. GC-MS *m*/*z* 79 (*cf.* for C_6H_6, 78).

Kinetic studies. For the transfer hydrogenation of benzaldehyde: 76 mmol Zn, 75 mmol benzaldehyde, 15 ml H_2O (or D_2O) and 0.3 mol% of Pd/C were stirred in a flask at 100 °C for 10 h. Periodic GC analysis gave the following k_{obs} values: $k_{\mathrm{H}} = 7.65 \times 10^{-2}$ h^{-1} ($r^2 = 0.999$ for 11 observations); $k_{\mathrm{D}} = 4.75 \times 10^{-2}$ h^{-1} ($r^2 = 0.9985$ for 11 observations). For the hydrogen generation reactions: 150 mmol zinc, 300 mmol H_2O (or D_2O or Mix1 or Mix2), 1 mol% Pd/C and 100 ml dry PhMe were stirred in an autoclave at 75 °C for 6 h. Periodic GC analysis gave the following k_{obs} values: $k_{\mathrm{H_2O}} = 6.2 \times 10^{-4}$ min^{-1} ($r^2 = 0.989$ for 12 observations); $k_{\mathrm{D_2O}} = 4.3 \times 10^{-5}$ min^{-1} ($r^2 = 0.99$ for 11 observations); $k_{\mathrm{Mix1}} = 6.1 \times 10^{-4}$ min^{-1} ($r^2 = 0.988$ for 11 observations); $k_{1,\mathrm{Mix2}} = 6.0 \times 10^{-4}$ min^{-1} ($r^2 = 0.99$ for 5 observations); $k_{2,\mathrm{Mix2}} = 4.2 \times 10^{-5}$ min^{-1} ($r^2 = 0.999$ for 8 observations).

Notes and references

§ Indeed, this is an exothermic reaction, $\Delta H_{\mathrm{r}}^0 = -14.9$ kcal mol^{-1}, and $\Delta G_{\mathrm{r}}^0 = -19.4$ kcal mol^{-1}.[7]

¶ 1 : 1 molar ratios can be used, but the reaction is much slower. Moreover, for effective stirring in the 300 ml autoclave a minimal volume is required. For these reasons, an excess (50–100 ml in this case) of water was used.

‖ The equilibrium constant for the reaction $H_2O + D_2O \rightleftharpoons HDO$ at 75 °C was reported[9] as $K_{\mathrm{eq}} = 3.12$. Therefore, Mix1 contains a 2 : 1 : 1 equilibrium ratio of HDO : D_2O : H_2O.

** This low isotope effect may be attributed to O–H (O–D) bond lengthening during the adsorption of the water molecule onto the catalyst.

†† The reaction $Pd + H_2O \rightleftharpoons PdO + H_2$ is thermodynamically unfavourable, with $\Delta G_r^0 > +30$ kcal mol^{-1}.[7]

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