# Hydrogen evolution from organic "hydrides"

**Daniel E. Schwarz, Thomas M. Cameron, P. Jeffrey Hay, Brian L. Scott, William Tumas and David L. Thorn***

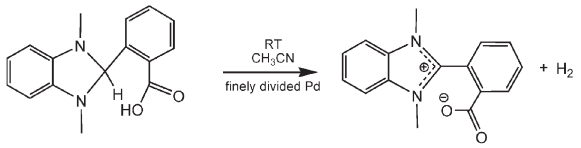
***Received (in Berkeley, CA, USA) 19th August 2005, Accepted 22nd September 2005***
***First published as an Advance Article on the web 20th October 2005***
**DOI: 10.1039/b511884k**

**Benzimidazolines (dihydrobenzimidazoles) are shown for the first time to eliminate hydrogen ($H_2$) by catalyzed reaction with protic compounds.**

Exergonic elimination of hydrogen (as $H_2$) from organic compounds under mild conditions is rare. For the vast majority of organic compounds, hydrogen elimination is strongly endothermic and endergonic at ambient temperature.[1] For example, $\Delta H^\circ$ for hydrogen elimination from decalin to form naphthalene[2] is 72 kJ per mole of $H_2$, and the equilibrium pressure of $H_2$ is less than one atmosphere unless the temperature is above *ca.* 275 °C. The dehydrogenation of common alcohols is likewise endothermic, and at ambient temperature occurs only in the presence of hydrogen acceptors[3] or in an open system where hydrogen does not accumulate to significant pressure.[4,5] Among the few examples of exergonic hydrogen elimination at ambient temperature, the most familiar is formic acid which forms $H_2$ and $CO_2$ rapidly in the presence of catalysts.[6–8] Other organic systems that evolve hydrogen spontaneously include formaldehyde in strong alkaline media,[9] aqueous aldehydes under modified hydroformylation conditions,[10] alkane C–H bonds in superacid media,[11] and protonated orthoformamide derivatives[12] at elevated temperatures.

We describe herein a new and gentle exergonic process for molecular hydrogen evolution from benzimidazolines (dihydrobenzimidazoles) that does not require strong acid, strong base, or other forcing conditions. Benzimidazolines are known to be relatively highly reduced/reducing organic species, and there is a rich redox chemistry associated with reactions involving *o*-phenylenediamine and aldehydes.[13] The only reported example of hydrogen evolution from dihydrobenzimidazoles occurs when they are combined with strong oxidizing agents $Ag^+$ or ferricyanide,[14] where it is believed that some hydrogen radicals ($H^\bullet$) are formed in strongly exothermic oxidation processes and $H_2$ is released in substoichiometric quantities. Stoichiometric, non-oxidatively-driven hydrogen evolution from dihydrobenzimidazole compounds has not been reported, although one research group made several deliberate and determined attempts to force hydrogen evolution from dihydrobenzimidazoles by reaction with intramolecular proton sources.[15] Because hydrogen was not found among the reaction products, the authors reluctantly came to the conclusion that dihydrobenzimidazoles are thermodynamically incompetent to react with acid to evolve hydrogen, despite being specially constructed so as to facilitate intramolecular hydrogen elimination.[15] Upon considering this system we suspected that the failure to eliminate hydrogen from dihydrobenzimidazole–acid combinations arises from an intrinsic kinetic barrier, not thermodynamic incompetence, and by studying the effects of catalysts we have demonstrated the exothermic and exergonic evolution of hydrogen at ambient temperature.

Following the literature report we prepared the *N*,*N*′-dimethyl dihydrobenzimidazole compound **1**[15] and confirmed it to be quite stable both in solution and in the solid-state at temperatures up to 80 °C, in the absence of air and catalyst. However, when treated with 3 mol% Pearlman's catalyst ($Pd(OH)_2$ on carbon) in acetonitrile at 80 °C, **1** lost $H_2$[16] with concomitant generation of the internal salt (2-(1,3-dimethylbenzimidazolium-2-yl)benzoate)[15] **2** (eqn. 1).




(1)

With other forms of palladium the catalytic transformation of **1** to **2** with $H_2$ evolution occurred at room temperature. When acetonitrile solutions of **1** were treated at room temperature with 5 mol% of $Pd(O_2CCH_3)_2$, $Pd(O_2CCF_3)_2$, or $K_2PdCl_4$ in acetonitrile suspensions/solutions, a black precipitate formed immediately, identified as finely divided $Pd^0$ by X-ray powder diffraction, rapidly followed by generation of **2** with effervescent $H_2$ evolution.

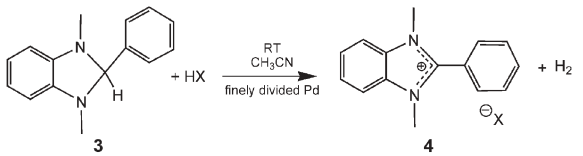
All reactions described herein were followed by NMR spectroscopy, and the transformations of organic reactants to the indicated products are very clean; acetic acid is also observed when palladium acetate is used as the palladium source in eqn. 1, and additional organic products are observed only for reactions involving water (*vide infra*). To confirm the evolution of $H_2$ in eqn. 1 the reaction headspace was exposed to a separate reaction chamber containing one equivalent of *trans*-stilbene and Pd catalyst at room temperature, and diphenylethane was found by NMR spectroscopic analysis in an amount corresponding to capturing 47% of the expected $H_2$. The solid-state structures of **1**·pyridine and **2** were confirmed by X-ray crystallography and will be reported separately.[17]

Formally, the hydrogen elimination from compound **1** can be viewed as reaction between a "hydride" comprising the unique CH of the imidazolidine moiety and a proton from the carboxyl group, mediated by catalyst in a manner yet to be determined.[18] Intermolecular reactivity consistent with this formalism is confirmed by reaction of 1,3-dimethyl-2-phenylbenzimidazoline **3**[19] with acetic acid or benzoic acid under an inert atmosphere in the presence of finely divided palladium to afford hydrogen (eqn. 2) and the phenylbenzimidazolium cation **4**.[14] The reaction in eqn. 2 was monitored by $^1H$ NMR spectroscopy and was complete

*Chemistry Division, MS J514, Los Alamos National Laboratory, Los Alamos, 87545, New Mexico, USA. E-mail: dthorn@lanl.gov*

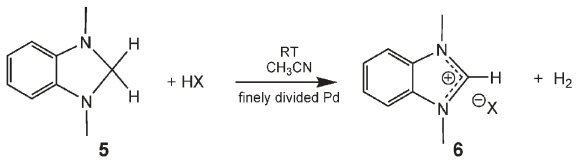
This journal is © The Royal Society of Chemistry 2005

within two hours at room temperature over Pd catalyst. Compound **3** is stable toward carboxylic acids for days at ambient temperature when no catalyst is present.



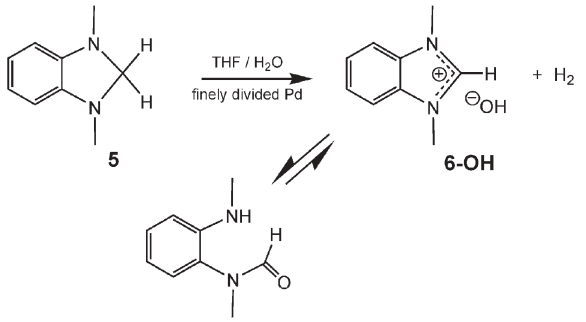

(2)

To determine whether the 2-phenyl group is required for the hydrogen elimination process, we prepared 1,3-dimethylbenzimidazoline **5**.[20] Compound **5** evolves gas (confirmed to be pure hydrogen by GC analysis) in the presence of carboxylic acid and catalyst, eqn. 3, similar to compound **3** but greater than 2x faster than compound **3** in competition experiments (palladium catalyst, HX = acetic acid). Wilkinson's catalyst, $RhCl(PPh_3)_3$, is a catalyst (or catalyst precursor) for hydrogen evolution from compound **5** according to eqn. 3, X = acetate, with a mean TOF of 117/hour at 70 °C.[21] (Under these conditions Wilkinson's catalyst does not effect hydrogen evolution from compounds **1** or **3**.) Compound **5** reacts slowly with carboxylic acids at elevated temperatures over the course of days when no hydrogen-evolving catalyst is present, largely by acid-promoted intermolecular disproportionation reactions[20] with little hydrogen formation. The solid-state structures of compound **6**, X = acetate and biacetate, have been confirmed by X-ray crystallography.[17]




(3)

We have not been able to reverse the hydrogen evolution in eqn. 1, eqn. 2, or eqn. 3 (HX = acetic acid) using Pd or $RhCl(PPh_3)_3$ catalyst nor determine the equilibrium pressure of hydrogen, but we note the following observations: (1) the reaction of eqn. 1 progresses to completion even under 3.5 atmospheres $H_2$ pressure; (2) *ab initio* calculations on the ambient-temperature transformation of **1** to **2** (eqn. 1) predict a strongly exergonic reaction in the gas phase at 298 K, $\Delta H = +7.1$ kJ mol$^{-1}$ and $\Delta G = -21.8$ kJ mol$^{-1}$;[22] and (3) preliminary calorimetric measurements establish the reaction of **5** with neat acetic acid at 310 K as exothermic by 44 ± 12 kJ mol$^{-1}$ (10 ± 3 kcal mol$^{-1}$). Thus hydrogen evolution is driven by both entropy and enthalpy, so ambient-temperature hydrogen evolution from benzimidazolidine compounds **1**, **3**, **5** and carboxylic acids is strongly exergonic ($\Delta G << 0$) and reversing the hydrogen evolution from these compounds by pressure alone will be extremely difficult. It follows that acids much weaker than carboxylic acids could still lead to hydrogen formation in eqn. 2 and eqn. 3, and we have confirmed that water is sufficiently acidic for Pd-catalyzed hydrogen evolution from compounds **3** and **5**. For example, the reaction of compound **5** in aqueous MeOH over palladium proceeds initially according to eqn. 3, but the rate of hydrogen evolution becomes very slow as hydroxide accumulates and the pH of the solution rises to a steady-state value of *ca.* 12.2. In a separate study using MeOH/water mixture buffered with carbonate/bicarbonate at nominal pH 10, the hydrogen evolution reaction over Pd (eqn. 3, HX = $H_2O/HCO_3^-$) reached 50% after 24 h at 70 °C. In other solvents, *e.g.* THF/water, the reaction becomes more complex owing to further reactions of hydroxide with benzimidazolium cations, with the initial reaction as in eqn. 4.[23,24]




(4)

These results demonstrate the existence of "organic hydride" systems that are sources of hydrolytically-releasable hydrogen, reminiscent of inorganic hydrides such as $NaBH_4$ and LiH. From the heat of reaction of acetic acid with **5** ($\Delta H$ *ca.* −44 ± 12 kJ mol$^{-1}$) and additional thermodynamic values indicated in Scheme 1, we *estimate* the "hydricity"[25] of **5** in the range +198 ±22 kJ (42–55 kcal). While there is considerable uncertainty this estimate predicts that **5** is appreciably more "hydridic" than several NADH analogs (hydridicities *ca.* +251 ± 8 kJ),[25] which is fully consistent with $H_2$ evolution from NADH (water, pH 7) being endergonic by 19 kJ mol$^{-1}$ (4.6 kcal mol$^{-1}$)[26] whereas $H_2$ evolution from **5** (water/methanol, pH 10) is exergonic at 70 °C.

| | |
|---|---|
| **5** + $HOOCCH_3$ = **6**-acetate + $H_2$ | ΔH = -44 +/- 12 kJ mol$^{-1}$<br>-TΔS = -30 +/- 10 kJ mol$^{-1}$ |
| $H^+$ + acetate$^-$ = $HOOCH_3$ | ΔG = -46 kJ mol$^{-1}$<br>(pK ca. 8 in $CH_3CN$)[27] |
| $H_2$ = $H^+$(sol) + $H^-$(sol) ($CH_3CN$) | ΔG = 318 kJ mol$^{-1}$ [28] |
| **5** = **6** + $H^-$(sol) | ΔG = 198 +/- 22 kJ mol$^{-1}$ |

**Scheme 1**

We are especially interested in the new opportunities for chemical hydrogen storage[29] presented by organic systems of this type, as promoters or carriers of stored hydrogen from some other medium or possibly as storage media themselves. By modifying these organic systems we anticipate achieving thermodynamically reversible hydrogen evolution and enabling more facile and efficient dehydrogenation/regeneration than is possible for inorganic hydrides. Because the density of hydrogen storage is extremely important, much lighter organic frameworks than compounds **1**, **3**, or **5** will be required before such systems become useful as primary storage media. A major emphasis of our ongoing research is maintaining favorable thermochemical and kinetic parameters for hydrogen evolution while lowering the molecular weight of the organic framework. Future work will also include detailed mechanistic studies and the development of more active heterogeneous and homogeneous catalysts for this process.

This work was supported as part of the DOE Center of Excellence for Chemical Hydrogen Storage through the Office of Energy Efficiency and Renewable Energy National Hydrogen Storage Project. T. M. C. thanks the Los Alamos National Laboratory for a Director Funded Postdoctoral Fellowship.

 This journal is © The Royal Society of Chemistry 2005

## Notes and references


1 See for example: (*a*) F. C. Liu, E. B. Pak, B. Singh, C. M. Jensen and A. S. Goldman, *J. Am. Chem. Soc.*, 1999, **121**, 4086–4087; (*b*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792; (*c*) N. Kariya, A. Fukuoka and M. Ichikawa, *Appl. Catal., A*, 2002, **233**, 91–102; (*d*) Other approaches to organic systems where endothermic dehydrogenation can be driven at mild temperature are described by G. P. Pez, A. R. Scott, A. C. Cooper, H. Cheng, *US Patent Application*, 20050002857 (A. C. Cooper, personal communication).

2 S. Hodoshima, H. Arai, S. Takaiwa and Y. Saito, *Int. J. Hydrogen Energy*, 2003, **28**, 1255–1262.

3 D. Morales-Morales, R. Redón, Z. Wang, D. W. Lee, C. Yung, K. Magnuson and C. M. Jensen, *Can. J. Chem.*, 2001, **79**, 823–829.

4 Y. Lin, M. Dawei and X. Lu, *Tetrahedron Lett.*, 1987, **28**, 3115–3118.

5 J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics*, 2004, **23**, 4026–4033.

6 Y. Gao, J. K. Kuncheria, H. A. Jenkins, R. J. Puddephatt and G. P. A. Yap, *J. Chem. Soc., Dalton Trans.*, 2000, 3212–3217.

7 R. Williams, R. S. Crandall and A. Bloom, *Appl. Phys. Lett.*, 1978, **33**, 381–383.

8 The microscopic reverse of formic acid dehydrogenation is the hydrogenation of carbon dioxide, see: (*a*) C. A. Thomas, R. J. Bonilla, Y. Huang and P. G. Jessop, *Can. J. Chem.*, 2001, **79**, 719–724; (*b*) C.-C. Tai, J. Pitts, A. D. Main, J. Linehan, P. Munshi and P. G. Jessop, *Inorg. Chem.*, 2002, **41**, 1606–1614; (*c*) P. Munshi, A. D. Main, J. Linehan, C.-C. Tai and P. G. Jessop, *J. Am. Chem. Soc.*, 2002, **124**, 7963–7971; (*d*) A. Baiker, *Appl. Organomet. Chem.*, 2000, **14**, 751–762 and references therein.

9 E. C. Ashby, F. Doctorovich, C. L. Liotta, H. M. Neumann, E. K. Barefield, A. Konda, K. Zhang and J. Hurley, *J. Am. Chem. Soc.*, 1993, **115**, 1171–1173.

10 G. G. Stanley, personal communication.

11 (*a*) G. A. Olah, Y. Halpern, J. Shen and Y. K. Mo, *J. Am. Chem. Soc.*, 1973, **95**, 4960–4970; (*b*) J. Sommer and J. Bukala, *Acc. Chem. Res.*, 1993, **26**, 370–376.

12 P. Brunet and J. D. Wuest, *J. Org. Chem.*, 1996, **61**, 2020–2026.

13 (*a*) T. Kondo, S. Yang, K.-T. Huh, M. Kobayashi, S. Kotachi and Y. Watanabe, *Chem. Lett.*, 1991, 1275–1278; (*b*) J. G. Smith and I. Ho, *Tetrahedron Lett.*, 1971, 3541–3544; (*c*) H. Chikashita, S. Nishida, M. Miyazaki, Y. Morita and K. Itoh, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 737–746.

14 A. S. Morkovnik, E. P. Ivakhnenko, Yu. G. Bogachev, B. A. Tertov, N. T. Berberova and O. Yu. Okhlobystin, *Khim. Geterotsikl. Soedin.*, 1988, **2**, 203–208.

15 P. Brunet and J. D. Wuest, *Can. J. Chem.*, 1996, **74**, 689–696; F. Mongrain, S. M. Ramos and J. D. Wuest, *J. Org. Chem.*, 1988, **53**, 1489–1492.

16 The initial evolution of hydrogen was reasonably rapid but catalyst deactivation was also occurring at a significant rate. Typically about half of the theoretical amount of hydrogen was evolved in the first 20 minutes.

17 D. E. Schwarz, T. M. Cameron, B. L. Scott, W. Tumas and D. L. Thorn, to be submitted for publication.

18 Homogeneous catalysts may operate by a polar mechanism analogous to the reverse of imine hydrogenation, see *e.g.*: (*a*) W. Fischer, R. T. Hembre, D. R. Sidler and J. R. Norton, *Inorg. Chim. Acta*, 1992, **198–200**, 57–61; (*b*) M. P. Magee and J. R. Norton, *J. Am. Chem. Soc.*, 2001, **123**, 1778–1779; (*c*) H. Guan, M. Iimura, M. P. Magee, J. R. Norton and K. E. Janak, *Organometallics*, 2003, **22**, 4084–4089.

19 A. Pandu Ranga Reddy, V. Veeranagaiah and C. V. Ratnam, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1985, **24**, 367–371.

20 A. V. El'tsov, *Zh. Obshch. Khim.*, 1967, **3**, 199–204.

21 0.2 M **5** in $CD_3CN$, 10x acetic acid, closed J. Young NMR tube (headspace adequate to keep gauge pressure less than 1 atm).

22 Thermochemical values were computed from optimized structures and frequencies in the gas phase using the B3LYP functional with a 6-31G* basis.

23 J. Bourson, *Bull. Soc. Chim. Fr.*, 1971, **1**, 152–159.

24 It is reported that **5** can be formed from **6** and water by disproportionation reactions not involving molecular $H_2$: A. A. Konstantinchenko, A. S. Morkovnik, A. F. Pozharskii and B. A. Tertov, *Khim. Geterotsikl. Soedin.*, 1985, **12**, 1694–1695.

25 W. W. Ellis, J. W. Raebinger, C. J. Curtis, J. W. Bruno and D. L. DuBois, *J. Am. Chem. Soc.*, 2004, **126**, 2738–2743.

26 See for example: C.-H. Wong, L. Daniels, W. H. Orme-Johnson and G. M. Whitesides, *J. Am. Chem. Soc.*, 1981, **103**, 6227–6228.

27 J. Barbosa, J. L. Beltran and V. Sanz-Nebot, *Anal. Chim. Acta*, 1994, **288**, 271–278.

28 C. J. Curtis, A. Miedaner, W. W. Ellis and D. L. DuBois, *J. Am. Chem. Soc.*, 2002, **124**, 1918–1925.

29 "Chemical hydrogen storage" is loosely defined as storing hydrogen in compounds or materials containing chemically bonded H atoms, from which $H_2$ is released by a chemical reaction. See for example: (*a*) G. Sandrock, *J. Alloys Compd.*, 1999, **293–295**, 877–888; (*b*) E. Fakioğlu, Y. Yürüm and T. N. Veziroğlu, *Int. J. Hydrogen Energy*, 2004, **29**, 1371–1376.