EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100093

Chemistry Europe
European Chemical
Societies Publishing

Acid- and Base-Catalyzed Hydrolytic Hydrogen Evolution from Diboronic Acid

Yi Wang+,[a] Jialu Shen+,[a] Yu Huang,[a] Xiang Liu,*[a] Qiuxia Zhao,[b] and Didier Astruc*[b]

The efficient production of H_2 from hydrogen-rich sources, particularly from water, is a crucial task and a great challenge, both as a sustainable energy source and on the laboratory scale for hydrogenation reactions. Herein, a facile and effective synthesis of H_2 and D_2 from only acid- or base-catalyzed metal-free hydrolysis of $B_2(OH)_4$, a current borylation reagent, has been developed without any transition metal or ligand. Acid-catalyzed H_2 evolution was completed in 4 min, whereas the base-catalyzed process needed 6 min. The large kinetic isotopic effects for this reaction with D_2O, deuteration experiments and mechanistic studies have confirmed that both H atoms of H_2 originate from water using either of these reactions. This new, metal-free catalytic system holds several advantages, such as high efficiency, simplicity of operation, sustainability, economy, and potential further use.

Introduction

Hydrogen-rich inorganic hydrides, metal hydrides, nanostructured materials, and chemical storage materials such as NH_3BH_3, $NaBH_4$ or related compounds based on boron[1] have been regarded as most promising for chemical hydrogen storage materials due to their high hydrogen content and easily storage as solids.[2] Typically, hydrolysis of NH_3BH_3, $NaBH_4$ or related boron compounds catalyzed by optimized transition-metal nanoparticles smoothly generates H_2 under ambient conditions.[3] On the other hand, several simple organic/inorganic compounds such as for instance ethanol and water have been shown to be useful in transfer hydrogenation, a very rich organic chemistry field.[4] Indeed, the transport and current laboratory use of explosive H_2 is dangerous and hazardous. In this respect, another commercially available class of boron compounds, diboronic acid and esters, B_2X_4 (X=OH and pinacolate, pin, respectively)[5] has shown great usefulness in organic synthesis,[6] in particular for hydrogenation and cross coupling with haloarenes producing arylboronic derivatives that are well known as precursors of C–C bonds upon Miyaura-Suzuki coupling.[7] These two diboron derivatives have indeed largely been used in transition-metal-catalyzed transfer hydrogenation of a variety of substrates using water as the hydrogen source,[8] and H_2 has been found as intermediate[9] or product[10] in some of these reactions.

The mechanism of H_2 formation from water whereby both hydrogen atoms from H_2 are provided by water is therefore clearly of different nature from those involving transition-metal catalyzed hydrolysis of NH_3BH_3 or $NaBH_4$ by which one H atom is provided from water and the other one from NH_3BH_3 or $NaBH_4$.[10] Moreover, several reports have also appeared showing useful substrate hydrogenation using these diboron compounds with water as the only hydrogen source in the absence of transition metal catalyst.[11] In a seminal article on the reactions of B_2Cl_4, Wartik and Apple had noted: "$B_2(OH)_4$ is a white solid which dissolved in a large excess of water to liberate traces of hydrogen. The rate of hydrogen evolution was increased somewhat by the addition of sulfuric acid and became quite rapid on the addition of sodium hydroxide".[12] In parallel, Schlesinger had demonstrated metal-free acid-catalyzed H_2 formation from $NaBH_4$, and, on the contrary, decrease of hydrolytic activity in basic medium,[13] and Xu et al had disclosed similar trends with hydrolytic H_2 production from NH_3BH_3.[14]

Given the interest in H_2 evolution and the above applications of these diboron reagents involving their hydrolysis and hydrogenation reaction, we have re-investigated the $B_2(OH)_4$ hydrolysis reaction in the absence of transition-metal catalyst. Here we report the metal-free acid-catalyzed and base-catalyzed H_2 evolution upon hydrolysis of diboronic acid, $B_2(OH)_4$. (Eq. 1). The mechanisms of these reactions are proposed based on kinetic studies including kinetic isotope effect (KIE) using D_2O, *in situ* tandem reactions and deuteration experiments. Compared to transition-metal nanoparticle-catalyzed hydrolysis of $B_2(OH)_4$, this catalytic system also holds several advantages, such as high efficiency, simplicity of operation, sustainability, economy and potential further use.

$$B_2(OH)_4 + 2\,H_2O \xrightarrow{\text{Acid or Base}} 2\,B(OH)_3 + H_2\uparrow \qquad (1)$$

---

[a] *Y. Wang,+ J. Shen,+ Y. Huang, Prof. Dr. X. Liu*
College of Materials and Chemical Engineering,
Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, Material Analysis and Testing Center
China Three Gorges University,
Yichang, Hubei 443002, China
E-mail: xiang.liu@ctgu.edu.cn
https://www.x-mol.com/groups/liu_xiang
[b] *Q. Zhao, Prof. Dr. D. Astruc*
ISM, UMR CNRS N° 5255, Univ. Bordeaux
351 Cours de la Libération, 33405 Talence Cedex, France
E-mail: didier.astruc@u-bordeaux.fr
http://astruc.didier.free.fr/

[+] *These authors have contributed equally to this work and should be considered as co-first authors.*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100093

Results and Discussion

Acid-catalyzed H_2 evolution

The study started with hydrogen evolution upon hydrolysis of diboronic acid (1.0 mmol) in the presence of 0.05 mol/L of H_2SO_4 at 30 °C and, in this way, H_2 was obtained in 92 % yield in 7 min. Then, it was found that Na_2SO_4 did not work, which indicates that the catalytic efficiency of H_2SO_4 is attributed to the protons (aq. H_3O^+). This acid-catalyzed diboronic acid hydrolysis has been kinetically evaluated by varying the concentrations in catalyst and diboronic acid and studying the temperature effect. H_2 evolution in this reaction has been carried out under various acid concentrations: 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 M (mol/L), while the initial diboronic acid concentration was kept constant at 0.5 M. Figure 1 shows the plots of time *vs.* volume of H_2 generated by acid-catalyzed diboronic acid hydrolysis at different catalyst concentrations at 30 °C and the plot of H_2 production rate *vs.* acid concentration in the logarithmic scale. The slope of 0.20 demonstrates that the acid-catalyzed hydrolysis of diboronic acid is first-order with respect to the catalyst concentration. In diboronic acid concentration-dependent hydrolysis, the acid concentration was kept at 0.5 M, while the diboronic acid amounts were set at 0.5, 0.75, 1.0 and 1.25 mmol, respectively. Figure 2 exhibits the plot of H_2 production rate vs. diboronic acid concentration in logarithmic scale. The slope of 0.92 indicates that the acid-catalyzed hydrolysis is also first-order with respect to the concentration of diboronic acid. Finally, to obtain the activation energy (E_a) of the H_2 production, diboronic acid (0.5 M) was hydrolyzed in the presence of 0.5 M sulfuric acid at various temperatures (from 303 K to 333 K). Figure 3 exhibits the plot of time vs. volume of H_2 generated during diboronic acid hydrolysis at various temperatures. The values of the rate constant k at different temperatures were calculated from the slope of the linear part of each plot for the determination of the activation energy, yielding the E_a value of 15.75 kJ/mol, based on the Arrhenius equation. HCl was also found to catalyze $B_2(OH)_4$ hydrolysis as well as H_2SO_4 with quantitative H_2 formation.

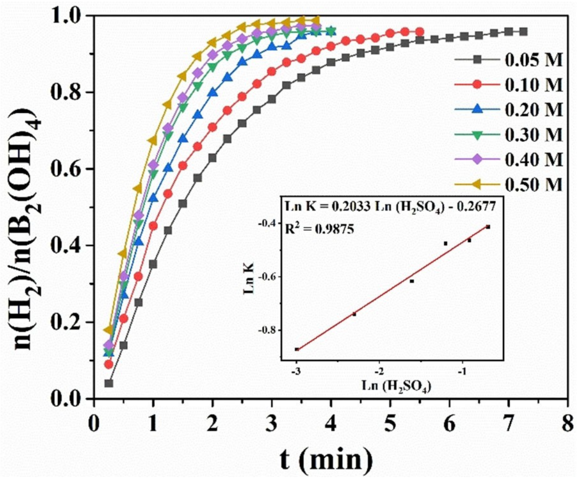


Figure 1. Time plots of the catalytic evolution of H_2 as a function of the H_2SO_4 concentration. Inset image: plots of the rates of H_2 generation *vs.* the concentration of H_2SO_4, both on natural logarithmic scales.

Base-catalyzed H_2 evolution

In a preliminary experiment, the H_2 evolution reaction has been initially conducted by using 1 mmol of $B_2(OH)_4$ in the presence of various amounts of Na_2CO_3 (from 0.2 mmol to 1.2 mmol) in water (2 mL) at 30 °C, and 1 mol H_2 *per* mol $B_2(OH)_4$ was produced (Figure 4a). The slope of the logarithmic plot of H_2 generation *vs.* concentration of Na_2CO_3 is 0.86, indicating that H_2 evolution is first order in catalyst concentration. Above 1 mmol Na_2CO_3, the catalytic efficiency of H_2 evolution no longer increased due to the saturation of the catalyst. Na_2SO_4

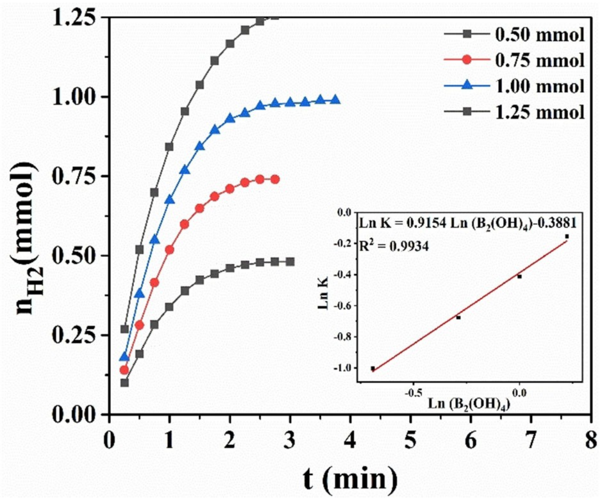


Figure 2. Plots of the volume of hydrogen generated *vs.* time for the H_2 evolution at various amount of $B_2(OH)_4$ (both on natural logarithmic scales).

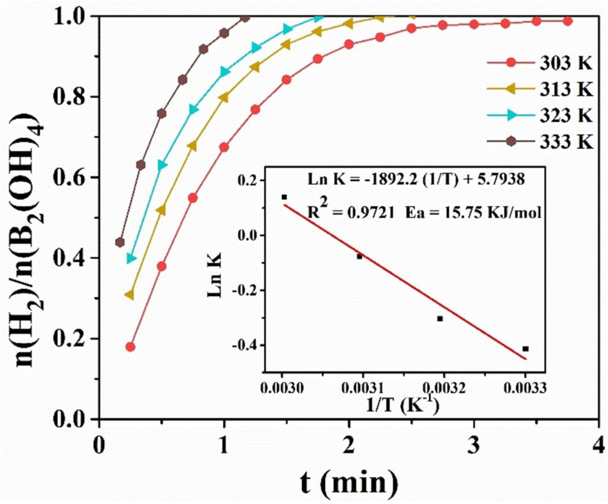


Figure 3. Plots of the hydrogen volume *vs.* time for evolution of H_2 catalyzed at various temperatures (both on natural logarithmic scales).

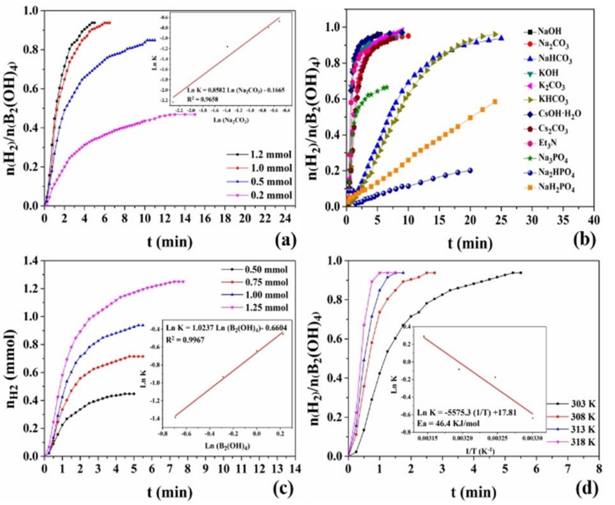


Figure 4. Comparison of H_2 evolution catalyzed by (a) various amounts of Na_2CO_3; (b) 1 mmol of different bases. (c) Time plots of the catalytic H_2 evolution by 1 mmol Na_2CO_3 in various concentrations of $B_2(OH)_4$. (d) Plots of the hydrogen volume *vs.* time for catalyzed H_2 evolution at various temperatures by Na_2CO_3; inset image: kinetic data obtained from the Arrhenius plots.

does not work for H_2 evolution, which shows that the catalytic efficiency of Na_2CO_3 is attributed to CO_3^{2-}. For comparison, NH_3BH_3, $NaBH_4$, B_2Pin_2 and $B(OH)_3$ have been tested for base-catalyzed H_2 evolution under the same conditions, and neither of these boron compounds works. Then, H_2 evolution from $B_2(OH)_4$ hydrolysis was carried out in the presence of 1 mmol of various bases (Figure 4b), and it was found that Et_3N, NaOH, Na_2CO_3, CsOH, Cs_2CO_3 and KOH are very efficient for H_2 evolution. The acidic bicarbonate salts $KHCO_3$ and $NaHCO_3$ are less efficient than their corresponding carbonates K_2CO_3 and Na_2CO_3, respectively. Na_2HPO_4 and NaH_2PO_4 are little efficient for this H_2 evolution reaction, indicating that the nature of the alkali metal cation does not significantly influence the reaction. These experiments are thus strongly in favor of OH^- as the active catalytic species for H_2 evolution and, in the case of non-hydroxide base, OH^- is provided from water upon reaction with carbonate. Then, the influence of the concentration of $B_2(OH)_4$ on H_2 evolution in the presence of 1 mmol of Na_2CO_3 has been investigated at 30 °C (Figure 4c).

The slope of the logarithmic plot of H_2 generation *vs.* concentration of $B_2(OH)_4$ was found to be 1.02, showing that H_2 evolution is first order in $B_2(OH)_4$ concentration. The efficiency of H_2 evolution at different reaction temperatures from 303 to 318 K is shown in Figure 4d. Based on the Arrhenius equation, the activation energy (Ea) value is 46.4 kJ/mol for Na_2CO_3.

Kinetic and mechanistic study

The isotopic experiment using D_2O instead of H_2O has been carried out for acid or base-catalyzed $B_2(OH)_4$ hydrolysis, and the kinetic results are shown in Figure 5, showing that the primary KIEs are 5.47 and 5.48 for acid and base-catalyzed H_2 evolution, respectively, strongly suggesting that the O–H bond of H_2O is cleaved in the rate-determining reaction step in both acid and base-catalyzed H_2 evolution.[15]

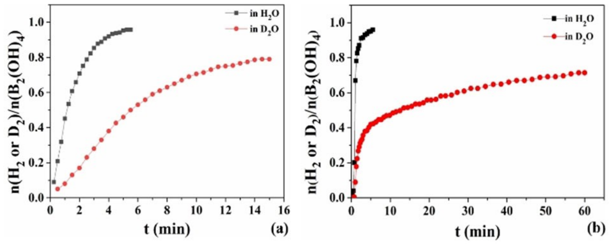


Figure 5. (a) Acid- and (b) base-catalyzed H_2 evolution in H_2O (black) or D_2O (red).

H_2 generated from the hydrolysis of $B_2(OH)_4$ reaction is not only utilized for hydrogen storage, but also for *in situ* tandem reactions, and for mechanistic study of the $B_2(OH)_4$ hydrolysis reaction. For further confirming hydrogen evolution from the diboronic acid hydrolysis reaction catalyzed by the acid catalyst, the tandem reaction for the hydrogenation diphenylacetylene, norbornene and 1,1-diphenylethylene with H_2 produced from diboronic acid hydrolysis catalyzed by sulfuric acid, the reaction was carried out in a sealed two-chamber system at 30 °C for 12 h (Scheme S1), and all the reactions of diphenylacetylene, norbornene and 1,1-diphenylethene hydrogenation provided 99 % yield of the desired products, confirming H_2 evolution from acid-catalyzed diboronic acid hydrolysis. In addition, the formation of $B(OH)_3$ was confirmed by ESI mass spectrometry (Figure S1), ^1H (Figure S2) and ^{11}B NMR (Figure S3) and XRD (Figure S4). Similarly, the tandem reactions for hydrogenation of norbornene and 1,1-diphenylethene with H_2 generated from $B_2(OH)_4$ hydrolysis catalyzed by Na_2CO_3 are represented in Scheme S2. Both hydrogenations of norbornene and 1,1-diphenylethene provided 99 % yield of the desired products, confirming the stoichiometric formation of H_2 upon base-catalyzed sealed two-chamber system (Figure 6), D_2 was generated from acid-catalyzed $B_2(OH)_4$ hydrolysis with D_2O, the reaction being catalyzed diboronic acid hydrolysis. Moreover, the mass spectrum (Figure S5) also confirmed the formation of the reaction product, $B(OH)_3$. In a by H_2SO_4 in the left chamber. This D_2 was utilized for the *in-situ* hydrogenation of norbornene catalyzed by commercial Pd/C in the right chamber. Then, the desired product **2f** was obtained in 99 % yield (Eq. 2), confirming that both H atoms of hydrogen are provided from water. In parallel, D_2 was also generated from base-catalyzed $B_2(OH)_4$ hydrolysis with D_2O, the reaction being catalyzed by Na_2CO_3 in the left chamber (Figure 7). This D_2 was utilized for the *in-situ* hydrogenation of norbornene catalyzed by Pd/C in the right chamber. Then, the desired product **2g** was obtained in 99 % yield (Eq. 3), also confirming that both H atoms of hydrogen are provided from water. For the hydrogenation of 1,1-diphenylethene (1c) with D_2, the methyl group was 49 % deuterated, whereas the benzylic position was only 51 % deuterated, which corresponds to a total incorporation of 1.98 D, close to the expected 2 D. (Eq. 4). The uneven distribution is due to the

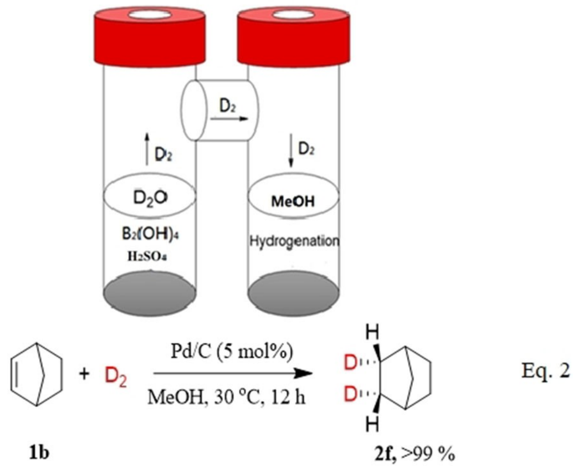


Figure 6. Tandem reaction for hydrogenation with D_2 generated from $B_2(OH)_4$ hydrolysis using D_2O catalyzed by H_2SO_4.

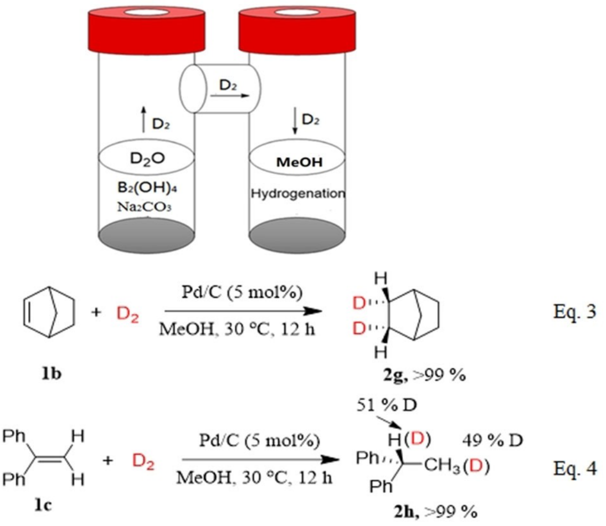


Figure 7. Tandem reaction for hydrogenation in which D_2 is generated from $B_2(OH)_4$ hydrolysis with D_2O catalyzed by Na_2CO_3.

facile H or D atom migration in the semi-hydrogenated radical species[16] between the benzylic and homobenzylic positions due to the preferred benzylic radical stabilization.

A mechanistic proposal of acid-catalyzed hydrolysis of $B_2(OH)_4$ reaction is shown in Figure 8. Initially, the intermediate **A** is formed by the interaction of H_3O^+ with $B_2(OH)_4$. Although oxidative addition of the B–B bond of diboron to d^8 metal is well known,[17] its protonation is less so. Subsequently, it gives intermediate **B** by capturing one H atom from H_2O. Then, the intermediate **C** is afforded by the interaction of **B** with H_3O^+. Next, **C** provides the intermediate **D** by capturing another H atom from water releasing H_2. Finally, **D** releases a molecule of $B(OH)_3$, which leads to completion of the catalytic cycle. In this mechanism, the formation of H_2 from **C** results from considerable structural reorganization upon σ-bond metathesis,[18] for which the large KIE value is taken into account.

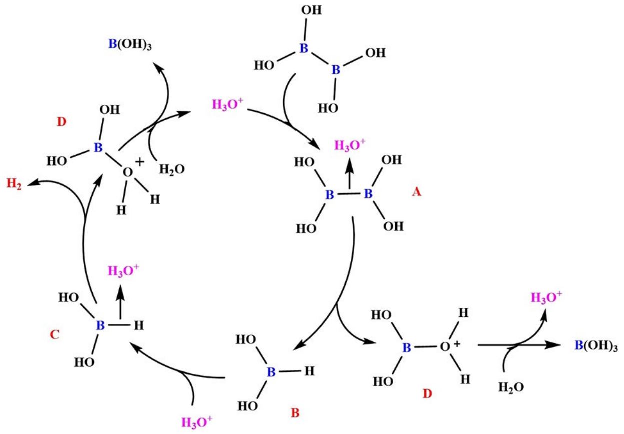


Figure 8. Proposed mechanism for the acid-catalyzed hydrolysis of $B_2(OH)_4$.

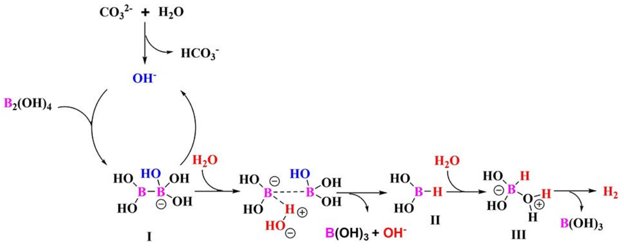


Figure 9. Proposed mechanism for the base-catalyzed hydrolysis of $B_2(OH)_4$.

For the base-catalyzed hydrolysis of $B_2(OH)_4$ reaction (Figure 9), the catalytic cycle starts with the formation of the intermediate **I** by attack of OH^- onto $B_2(OH)_4$. The intermediate **II** is then produced by protonation of the anion **I** by water and release of $B(OH)_3$. Subsequently, intermediate **III**, obtained by hydrolysis of **II**, decomposes to $B(OH)_3$ and H_2. Reductive elimination of H_2 from the B–O sites of **III** involves an important structural reorganization that is taken into account by the observed large primary KIE value.

Conclusion

In summary, metal-free acid- or base-catalyzed H_2 evolution is reported to proceed upon hydrolysis of $B_2(OH)_4$, in which both H atoms are obtained from water. $B_2(OH)_4$ is a frequently used borylation reagent and also sometimes in hydrogenation, thus the present findings are useful. Other boron compounds, such as NH_3BH_3, $NaBH_4$, B_2Pin_2 and $B(OH)_3$, do not work for base-catalyzed H_2 evolution in the absence of transition-metal nanoparticles, and in particular attempts to catalyze H_2 evolution upon base catalysis from all these reagents failed.

The large primary KIEs disclosed, $k_H/k_D = 5.47$ resp. $k_H/k_D = 5.48$, for acid and base-catalyzed H_2 evolution from $B_2(OH)_4$, respectively, with D_2O, confirmed water O–H bond cleavage as the rate- determining step for both reactions, and thus mechanisms are proposed (Figure 8 and Figure 9). The tandem reactions with D_2O that involves $B_2(OH)_4$ hydrolysis, norbornene and 1,1-diphenylethene hydrogenation have confirmed the formation of D_2. Note that these reactions in D_2O also provide easy and useful syntheses of D_2. Based on the Arrhenius equation, the activation energy E_a is 15.75 kJ/mol and 46.4 kJ/mol for H_2SO_4 and Na_2CO_3, respectively.

In sum, this system has the potential to achieve metal-free production and utilization of hydrogen, in spite of the fact that only one H_2 molecule is provided for each $B_2(OH)_4$ molecule. A serious drawback is the difficulty of reconverting diboronic acid from $B(OH)_3$, but this problem also is the same for the other hydride-rich boron derivatives such NH_3BH_3 and $NaBH_4$. Recent impressive progress has been accomplished along this line, however,[19] and catalyzed $B_2(OH)_4$ hydrolysis is therefore becoming an excellent method to conveniently and stoichiometrically generate H_2 at the laboratory scale.

Experimental Section

Chemicals and reagents. All commercial materials were used without further purification, unless indicated. The deionized water was prepared in the laboratory. $B_2(OH)_4$, Et_3N, NaOH, Cs_2CO_3, K_2CO_3, $CsOH.H_2O$, KOH, Na_3PO_4, Na_2CO_3, $NaHCO_3$, $KHCO_3$, Na_2HPO_4, NaH_2PO_4, BH_3NH_3, $NaBH_4$, D_2O, CD_3OD, Pd/C, B_2Pin_2 and $B(OH)_3$ were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China, http://www.aladdin-e. com/).

Acid-catalyzed evolution of H_2 upon reaction between $B_2(OH)_4$ and H_2O. Generally, the evolution of H_2 upon reaction between $B_2(OH)_4$ and H_2O was conducted in water at 30 °C. In a round-bottom 10-mL flask, 1.0 mmol of $B_2(OH)_4$ was added. A solution of H_2SO_4 (0.5 mol/L, 2 mL) is injected into this flask, and timing started. The flask was fitted with a gas outlet, and a side arm was sealed with a tight-fitting septum cap. The flask was connected via the gas outlet to a water-filled gas burette. Gas evolution immediately began, and the amount of gas evolved was determined periodically by measuring the displacement of water in the burette. A quantitative conversion of $B_2(OH)_4$ produced 1.0 equivalents of H_2, and occupied ca. 22.4 mL at atmospheric pressure. Prior to the reactions, the volumes were measured at atmospheric pressure and corrected for water vapor pressure at room temperature.

Base-catalyzed evolution of H_2 upon reaction between $B_2(OH)_4$ and H_2O. The reactions were conducted as above, except that the H_2SO_4 solution was replaced by NaOH (1.0 mmol, 2 mL).

The hydrogenation of diphenylacetylene, norbornene and 1,1-diphenylethylene. The tandem reaction was carried out in the sealed two-chamber system. The left tube was used for hydrogen generation, and the right one was used for hydrogenation with H_2 generated in the left tube. The generated hydrogen in the left tube transported to the hydrogenation reaction into the right tube through the connecting glass tube.

Acknowledgements

Financial support from the National Natural Science Foundation of China (21805166), the 111 Project (D20015), the Engineering Research Center of Eco-environment in Three Gorges Reservoir Region, Ministry of Education, China Three Gorges University (KF2019-05) and the outstanding young and middle-aged science and technology innovation teams, Ministry of Education, Hubei province, China (T2020004), Chinese Scientific Council (PhD grant to QZ), Université de Bordeaux and Centre National de la Recherche Scientifique (CNRS) is gratefully acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Acid catalysis · Base catalysis · Boron · Hydrogen evolution · Reaction mechanisms

[1] Z. G. Huang, S. N. Wang, R. D. Dewhurst, N. V. Ignat'ev, M. Finze, H. Braunschweig, *Angew. Chem. Int. Ed.* **2020**, *59*, 8800–8816.

[2] a) A. Staubitz, A. P. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124; b) T. He, P. Pachfule, H. Wu, Q. Xu, P. Chen, *Nat. Rev. Mater.* **2016**, *1*, 16059; c) C. Wang, D. Astruc, *Chem. Soc. Rev.* **2021**, https://doi.org/10.1039/D0CS00515 K; d) J. Zhou, Y. Huang, J. Shen, X. Liu, *Catal. Lett.* **2021**, https://doi.org/10.1007/s10562-021-03547-2.

[3] a) Q.-L. Zhu, Q. Xu, *Energy Environ. Sci.* **2015**, *8*, 478–512; b) W.-W. Zhan, Q.-L. Zhu, Q. Xu, *ACS Catal.* **2016**, *6*, 6892–6905; c) B. J. Zhu, R. Q. Zou, Q. Xu, *Adv. Energy Mater.* **2018**, *8*, 1801193; d) J. Shen, W. Chen, G. Lv, Z. Yang, J. Yan, X. Liu, Z. Dai, *Int. J. Hydrogen Energy* **2021**. *46*, 796–805; e) C. Wang, J. Tuninetti, Z. Wang, C. Zhang, R. Ciganda, L. Salmon, S. Moya, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2017**, *139*, 11610–11615; f) F. Fu, C. Wang, Q. Wang, A. M. Martinez-Villacorta, A. Escobar, H. Chong, X. Wang, S. Moya, L. Salmon, E. Fouquet, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2018**, *140*, 10034–10042; g) Q. Wang, F. Fu, S. Yang, M. M. Moro, M. de los Angeles Ramirez, S. Moya, L. Salmon, J. Ruiz, D. Astruc, *ACS Catal.* **2019**, *9*, 1110–1119; h) C. Wang, Q. Wang, F. Fu, D. Astruc, *Acc. Chem. Res.* **2020**, *53*, 2483–2493; i) Q. Yao, K. Yang, X. Hong, X. Chen, Z.-H. Lu, *Catal. Sci. Technol.* **2018**, *8*, 870–877; j) K. Wang, Q. Yao, S. Qing, Z.-H. Lu, *J. Mater. Chem. A* **2019**,*7*, 9903–9911; k) Q. Yao, Y. Ding, Z.-H. Lu, *Inorg. Chem. Front.* **2020**, *7*, 3837–3874.

[4] D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115*, 6621–6686.

[5] a) T. Wartik, E. F. Apple, *J. Am. Chem. Soc.* **1955**, *77*, 6400; b) R. A. Baber, N. C. Norman, A. G. Open, J. Rossi, *New J. Chem.* **2003**, *27*, 773–775; c) E. C. Neeve, S. J. Geier, I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.* **2016**, *116*, 9091–9161.

[6] a) D. S. Matteson, *Tetrahedron.* **1989**, *45*, 1859–1885; b) T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508–7510; c) V. J. Olsson, S. Sebelius, N. Selander, K. J. Szabo, *J. Am. Chem. Soc.* **2006**, *128*, 4588–4589.

[7] a) L. T. Pilarski, K. J. Szabo, *Angew. Chem. Int. Ed.* **2011**, *50*, 8320–8332; b) A. Zernickel, W. Du, S. A. Ghorpade, D. N. Sawant, A. A. Makki, N. Sekar, J. Eppinger, *J. Org. Chem.* **2018**, *83*, 1842–1851.

[8] a) V. Gurram, H. K. Akula, R. Garlapati, N. Pottabathini, M. M. Lakshman, *Adv. Synth. Catal.* **2015**, *357*, 451–462; b) D. P. Ojha, K. Gadde, K. R. Prabhu, *Org. Lett.* **2016**, *18*, 5062–5065; c) S. P. Cummings, T. N. Le, G. E. Fernandez, L. G. Quiambao, B. J. Stokes, *J. Am. Chem. Soc.* **2016**, *138*, 6107–6110; d) M. Flinker, H. Yin, R. W. Juhl, E. Z. Eikeland, J. Overgaard, D. U. Nielsen, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2017**, *56*, 15910–15915; e) Q. Q. Xuan, Q. L. Song, *Org. Lett.* **2016**, *18*, 4250–4253; f) X. Han, J. Hu, C. Chen, Y. Yuan, Z. Shi, *Chem. Commun.* **2019**, *55*, 6922–6925; g) N. N. Shaikh, *RSC Adv.* **2019**, *9*, 28199–28206; h) N. N. Shaikh, M. A. Aziz, A. N. Kalanthoden, A. Helal, A. S. Hakeem, M. Bououdina, *Catal. Sci. Technol.* **2018**, *8*, 4709–4717; i) K. A. Korvinson, H. K. Akula, C. T. Malinchak, D. Sebastian, W. Wei, T. A. Khandaker, M. R. Andrzejewska, B. Zajc, M. K. Lakshman, *Adv. Synth. Catal.* **2020**, *362*, 166–176; j) A. M. Gates, W. L. Santos, *Synthesis.* **2019**, *51*, 4619–4624; k) Y. Wei, C. Zhao, Q. Xuan, Q. Song, *Org. Chem. Front.* **2017**, *4*, 2291–2295; l) D. Pi, H. Zhou, Y. Zhou, Q. Liu, R. He, G. Shen, Y. Uozumi, *Tetrahedron.* **2018**, *74*, 2121–2129.

[9] S. K. Pedersen, H. G. Gudmundsson, D. U. Nielsen, B. S. Donslund, H. C. D. Hammershøj, K. Daasbjerg, T. Skrydstrup, *Nat. Catal.* **2020**, *3*, 843–850.

[10] W. F. Chen, J. L. Shen, Y. P. Huang, X. Liu, D. Astruc, *ACS Sustainable Chem. Eng.* **2020**, *8*, 7513–7522.

[11] a) Y. T. Xia, X. T. Sun, L. Zhang, K. Luo, L. Wu, *Chem. Eur. J.* **2016**, *22*, 17151–17155; b) Q. Xuan, C. Zhao, Q. Song, *Org. Biomol. Chem.* **2017**,

15, 5140–5144; c) Y. Huang, K. Zheng, X. Liu, X. Meng, D. Astruc, *Inorg. Chem. Front.* **2020**, *7*, 939–945; d) D. Chen, Y. Zhou, H. Zhou, S. Liu, Q. Liu, K. Zhang, Y. Uozumi, *Synlett.* **2018**, *29*, 1765–1768.

[12] T. Wartik, E. F. Apple, *J. Am. Chem. Soc.* **1958**, *80*, 6155–6158.

[13] H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, E. K. Hyde, *J. Am. Chem. Soc.* **1953**, *75*, 215–219.

[14] S. Liu, Y. Zhou, Y. Sui, H. Liu, H. Zhou, *Org. Chem. Front.* **2017**, *4*, 2175–2178.

[15] M. Chandra, Q. Xu, *J. Power Sources.* **2006**, *159*, 855–860.

[16] P. Michaud, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 918–919.

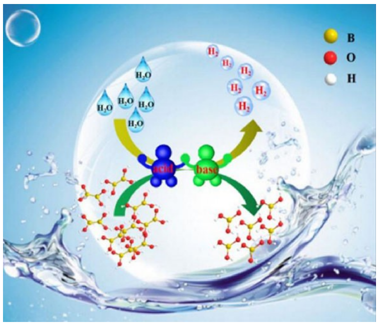
[17] H. E. Burks, S. Liu, J. P. Morken, *J. Am. Chem. Soc.* **2007**, *129*, 8766–8773.

[18] D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Berlin, **2007**, Chapter 3.

[19] Y. Zhu, L. Ouyang, H. Zhong, J. Liu, H. Wang, H. Shao, Z. Huang, M. Zhu, *Angew. Chem. Int. Ed.* **2020**, *59*, 8623–8629.

Manuscript received: February 4, 2021
Revised manuscript received: March 1, 2021
Accepted manuscript online: March 2, 2021

Metal-free H_2 or D_2 evolution is obtained in a few minutes from acid- or base-catalyzed hydrolysis of diboronic acid, respectively, under ambient conditions and is coupled to hydrogenation reactions. Kinetic studies allow proposing mechanisms by considering primary kinetic isotope effects observed for both acid- and based-catalyzed reactions with D_2O.



Y. Wang, J. Shen, Y. Huang, Prof. Dr. X. Liu, Q. Zhao, Prof. Dr. D. Astruc**

1 – 7

Acid- and Base-Catalyzed Hydrolytic Hydrogen Evolution from Diboronic Acid