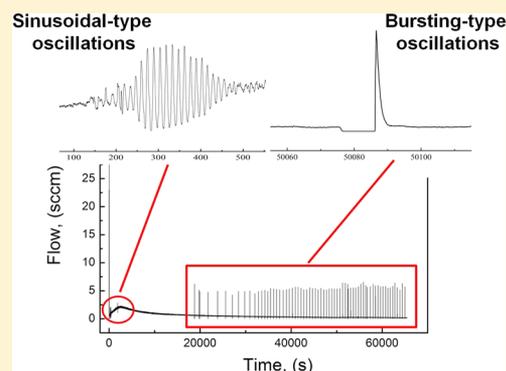


# Bursting Dynamics in Molecular Hydrogen Generation via Sodium Borohydride Hydrolysis

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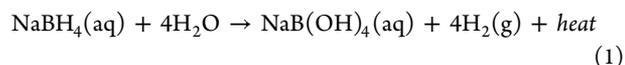
**ABSTRACT:** The hydrolysis of borohydride salts is a promising process for the generation in situ of pure molecular hydrogen that can be used as an alternative fuel. One of the obstacles toward its concrete application in the realm of green energy resides in nonlinear behaviors of H<sub>2</sub> delivery during the reaction development. In particular, we have recently shown that this system behaves like a chemical oscillator in a wide range of experimental conditions, exhibiting nondesirable fluctuations in the production of molecular hydrogen. Despite the potential of NaBH<sub>4</sub> hydrolysis in applicative terms, a deep understanding of the reaction mechanisms leading to these nonlinear dynamics is still left to a primary stage. Here we show how to control a typical bursting-like oscillatory scenario occurring in the gas development from NaBH<sub>4</sub> hydrolysis. Bursting transients are isolated and stabilized by using highly concentrated solutions of dihydrogen-phosphate/hydrogen-phosphate buffers with an initial pH value around 7. The length of the bursting transients critically depends upon the initial pH, the buffering strength, and the working temperature. The stirring rate also influences this oscillatory dynamics. On the basis of the experimental evidence and NMR analysis of the reactive mixture, we hypothesize a possible kinetic scheme able to explain the onset of oscillatory instabilities.



## INTRODUCTION

Transversal opinion is that we are at a critical point in terms of energy. On the one side much scientific evidence indicates that the exponential use of fossil resources increases CO<sub>2</sub> and other greenhouse gases in the atmosphere, thus provoking an increasing global warming and climate changes.<sup>1</sup> In parallel, there is a serious concern related to this massive exploitation of fossil fuels, which, in turn, may be not available in the long period to satisfy the energy demand. Despite the urgent need for alternative and green solutions to this energetic issue, no unique resolved pathway has been proposed but rather a pool of partial solutions. Among these, molecular hydrogen is one of the most concrete and promising. Molecular hydrogen can be easily converted into energy by using PEM fuel cells thanks to its oxidation with air, giving water as the main byproduct. Also, differently from other renewable sources of energy, molecular hydrogen can be stocked and stored to be used when needed. Nevertheless a hydrogen-based energy economy has not taken off due to important drawbacks. First, hydrogen has to be produced from other substances, and, typically, hydrogen generation is itself a source of greenhouse gases (consider, for instance, steam-reforming processes). From the engineering viewpoint, H<sub>2</sub> storage is also a challenging task, as it may involve pressurized containers with the gas extremely compressed or liquefied, thus introducing safety problems. In this context, chemical compounds and, specifically, boron hydrides have met growing interest as a possible solution to the problem

of hydrogen storage.<sup>2,3</sup> Among borohydride systems, sodium borohydride, NaBH<sub>4</sub>, is viewed with interest because of its considerable hydrogen gravimetric capacity, high stability in air, and low price. Hydrogen generation via NaBH<sub>4</sub> follows two main routes: thermolysis and hydrolysis. The latter, globally described by the reaction



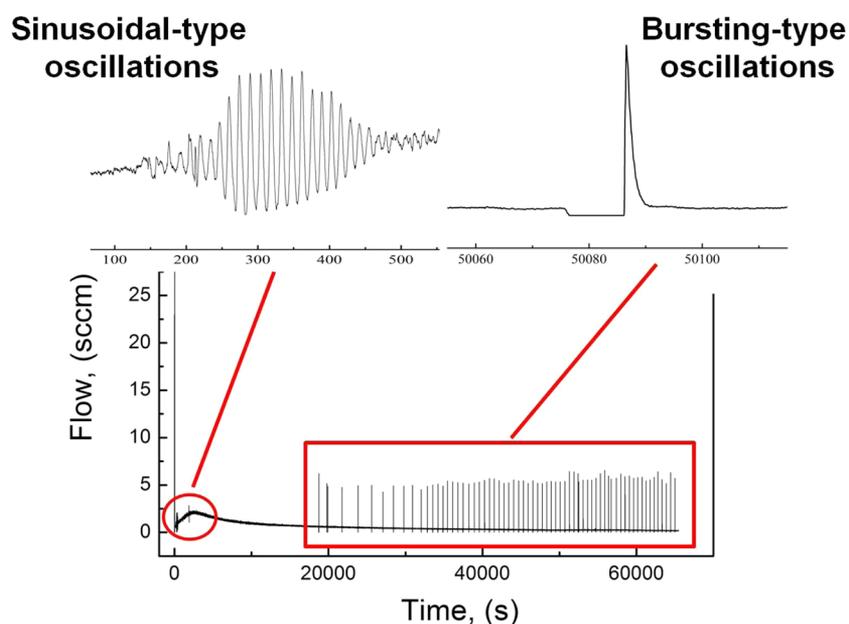
is a spontaneous and exothermic reaction that works under mild conditions.<sup>4</sup> This process yields environmentally safe byproducts (in particular, borates that can be recycled) and features a convenient strategy for in situ generation of highly pure hydrogen that can be used as a green fuel.<sup>5</sup>

Although reaction 1 appears to be an elementary process, it can present high kinetic complexity and different practical problems, undesirable for potential applications. One is the low solubility of NaBH<sub>4</sub> and of hydrated sodium metaborate (NaBO<sub>2</sub>),<sup>6</sup> which implies that a significant amount of water is needed to conduct the reaction efficiently. A second issue is connected to the slow reaction rate that calls for the use of proper catalysts to decrease the activation energy and accelerate the hydrogen generation rate under controlled conditions. A

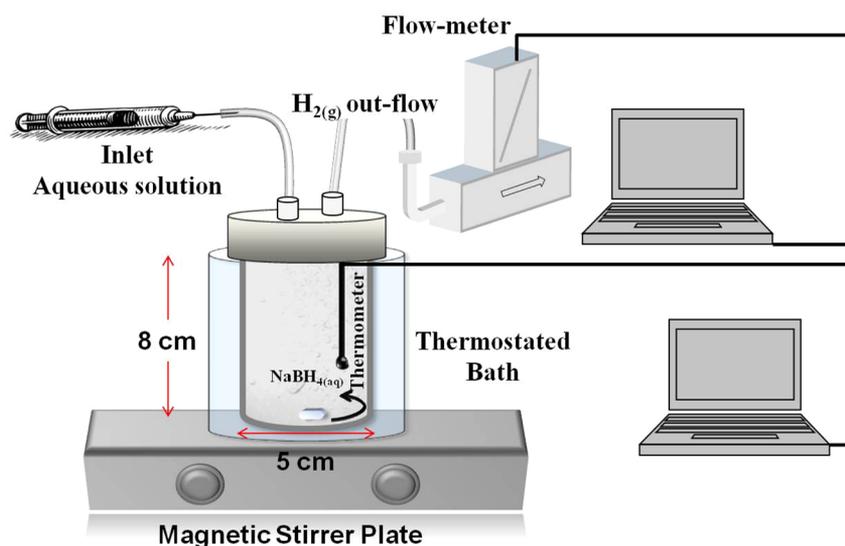
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**Figure 1.** Example of gaseous  $\text{H}_2$  out-flow in the noncatalyzed  $\text{NaBH}_4$  hydrolysis carried out with 1.5 g of  $\text{NaBH}_4$  and 15 mL of distilled water (i.e.,  $c_{\text{NaBH}_4} = 2.6 \text{ M}$ ) at  $30 \text{ }^\circ\text{C}$ . The dynamics can show two typical oscillatory scenarios: a sinusoidal-type transient and a bursting-type regime. Flow is given in standard cubic centimeters per minute (sccm).



**Figure 2.** Sketch of the experimental setup.

further problem is represented by nonlinear phenomena that can occur during the development of the reaction.<sup>7,8</sup> Although never instigated in depth, long-lasting periodic and more complicated oscillations have been shown in previous works where  $\text{NaBH}_4$  hydrolysis is performed under open conditions and in the presence of homogeneous catalysts such as nickel complexes.<sup>9–11</sup> Although many efforts have been devoted to enlighten the mechanism of the reaction,<sup>12–16</sup> important kinetic details that can explain the onset of oscillatory behaviors are still scarcely understood.

Recently we have systematically undertaken a kinetic study of  $\text{NaBH}_4$  hydrolysis and shown that the noncatalyzed hydrolysis can also exhibit oscillatory transients in the hydrogen generation.

Figure 1 illustrates a time series of the gas delivered during  $\text{NaBH}_4$  hydrolysis reaction, where two main oscillatory

scenarios characterizing this system can be observed. One is a sinusoidal-type periodic transient that takes place at the very beginning of the process (after 150–200 s). This dynamics typically consists of  $\sim 10$  oscillations with a characteristic period of  $18 \pm 2 \text{ s}$  and an amplitude ranging between 0.5 and 2 sccm. The second scenario is a long-lasting bursting-type regime in which the oscillation pattern shows an initial decrease in the gas-flow, followed by a spike and then a relaxation phase. The amplitude of these oscillations is much larger than that observed in the sinusoidal-type scenario (it ranges between 5 and 20 sccm under the reaction conditions considered).

In a previous study<sup>17</sup> we focused on the sinusoidal-type transient. Thanks to a series of ad hoc experiments we gave evidence that this oscillatory behavior is not the result of any instrumental artifices or stochastic fluctuations but it rather features a deterministic phenomenon that can be interpreted in

the framework of nonlinear chemistry. We investigated the nature of these oscillations and we could disprove the possibility that flow oscillations were fueled by physical mechanisms such as supersaturation that triggers gas oscillations in gas evolution oscillators (or bubblelator)<sup>18,19</sup> or by a thermokinetic interplay. Also, we could infer that gas flow oscillations are most probably driven by a chemical “oscillophor” in the reactive mixture.<sup>20,21</sup>

While sinusoidal-type transients were controlled and characterized to a large extent, bursting-like scenarios were found to be far less reproducible. In this work we isolate conditions for stabilizing and controlling these oscillatory regimes. We deepen the role of the reactive mixture pH and the temperature as critical parameters for the onset and the length of bursting regimes. On the basis of analytical investigations, we finally propose a minimal mechanism that may explain the onset of oscillatory instabilities in this system.

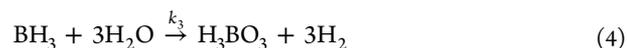
## EXPERIMENTAL SECTION

Experiments were carried out under batch conditions in a 25 mL quartz (or plexiglass) cylindrical reactor (see a schematic of the setup in Figure 2). We used different quantities of NaBH<sub>4</sub> (98% Sigma-Aldrich, powder) in a fixed volume (15 mL) of fresh prepared NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> pH buffers. Buffer solutions were prepared by using 1.00 M solutions of NaH<sub>2</sub>PO<sub>4</sub> and adding a proper volume of a 5.00 M NaOH solution to achieve the desired pH value. All reactants were commercial grade and used without any further purification. Stock solutions of NaH<sub>2</sub>PO<sub>4</sub> and NaOH were prepared by weight before use. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ, was used to prepare all solutions. NaBH<sub>4</sub> was kept under an argon atmosphere (specifically in a glovebox) to avoid the aging of the salt due to hydration. NaBH<sub>4</sub> fine powder was loaded into the reactor under an argon atmosphere, and the buffer solution was successively injected with a syringe from a valve placed at the top of the reactor. The reactive mixture was thermostated in a water bath. Typical experiments were performed at 30 ± 1 °C. However, various working temperatures have been considered and different stirring rates were applied to the solution via a programmable magnetic stirrer. The gas developed by NaBH<sub>4</sub> hydrolysis was piped through a Teflon tube into a flow-meter (Bronkhorst F-101, 0.1%FS accuracy) interfaced with a personal computer that allows us to follow the flow dynamics. We also monitored the solution and the bath temperature by means of two thermocouples. The dynamical profiles of the solution and the bath temperature were collected by means of an acquisition card (National Instruments) interfaced with a second PC.

<sup>11</sup>B NMR analyses were performed by using a quartz tube to avoid possible interferences of glass-made tubes in the detection of boron-based species. The solution for NMR analysis was prepared by using 3 mL of water (90 wt % H<sub>2</sub>O and 1 wt % D<sub>2</sub>O) and 0.5 g of NaBH<sub>4</sub>. The percent of deuterated water should be limited because it enhances and modifies the hydrolysis kinetics. Water was poured into the quartz NMR-tube immediately before the analysis start. Gas evolution does not affect significantly the quality of the spectrum.

## EXPERIMENTAL RESULTS

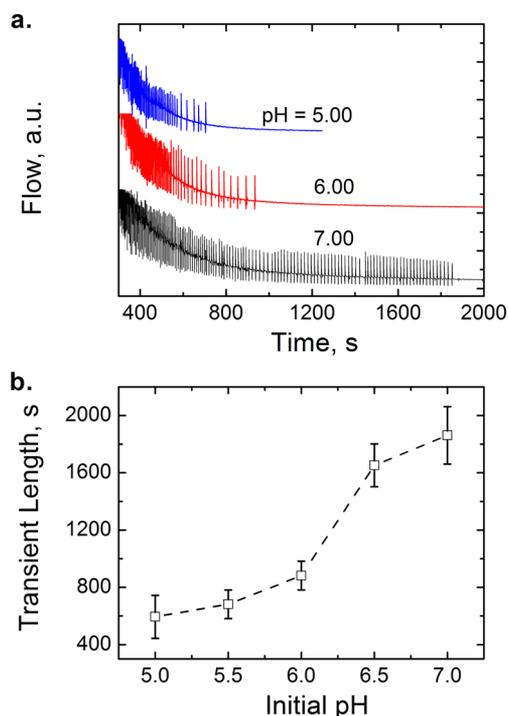
**Influence of the pH.** NaBH<sub>4</sub> hydrolysis and the related production of gaseous molecular hydrogen are strictly sensitive to the solution pH. To be more precise, the process is favored under acidic conditions and inhibited in a highly alkaline environment (pH >10.5). In the absence of any buffering, as the reaction is initiated, the pH of the system increases from a weakly acidic range to the interval 9.00 to 10.5, where the pH variation is much slower. The dependence of H<sub>2</sub> generation on the pH in borohydrides hydrolysis is embedded in the classical kinetic scheme used to describe the reaction<sup>12–14</sup>



where H<sub>3</sub>BO<sub>3</sub> progressively converts into sodium metaborate and tetrahydroborate while pH increases. It can be observed that H<sup>+</sup> fuels the conversion of NaBH<sub>4</sub> into molecular hydrogen. Intuitively the pH of the reactive mixture and its change in time also play a role in the oscillatory instabilities. In our previous investigations we already tried to understand how the solution pH impacts the onset of the oscillations and whether buffering the solution pH can stabilize oscillatory transients. To this aim, we followed the dynamics of the reaction performed in alkaline buffers (pH range [9.70, 11.50]) by using carbonate-bicarbonate pH buffers. MgCO<sub>3</sub> is, in fact, present as an anticaking agent in the NaBH<sub>4</sub> powder at hands (0.4 to 0.8%) and could act as a buffer in the reaction mixture. As expected, no oscillations were found by using buffer solutions with a pH >10.50. However, we could not find any characteristic oscillatory behavior even by buffering the system below pH 10.00, where regular oscillations were supposed to develop.

In this work we deepen the effect of pH as a critical parameter and stabilizing agent for oscillations by using a different buffer, namely the NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> system. This pH buffer allows us to work with more acidic initial pH values, typically in the range 5.00–8.00 (the pK<sub>a</sub> of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is ~7.2). Furthermore, as compared with our previous exploration, we use more concentrated buffer solutions (~1 M) to increase the pH buffering strength of the reactive solution. The solubility of NaBH<sub>4</sub> is not significantly affected by this fact.

In Figure 3a we resume the typical dynamics obtained when the reaction is performed with 1.5 g of NaBH<sub>4</sub> and 15 mL of 1 M NaH<sub>2</sub>PO<sub>4</sub>/Na<sub>2</sub>HPO<sub>4</sub> buffer solution (i.e., c<sub>NaBH<sub>4</sub></sub> = 2.6 M) at 30 °C and under 1000 rpm stirring. The introduction of the buffer critically affects the process evolution. In particular, it triggers the onset of gas oscillations, which start immediately upon injection of the buffer solution. Under these conditions bursting-type regimes can be isolated with a high reproducibility. The initial pH of the buffer solution can change the characteristics of the oscillatory pattern and the dynamics. Although the time series is strongly nonstationary (oscillations rely on a decreasing baseline), due to reactant consumption, we can clearly observe that the length of the bursting transient increases by increasing the initial pH in the range [5.00, 7.00] and becomes maximal around pH 7. This trend, quantitatively analyzed in Figure 3b, can be ascribed to the maximal buffering strength of the solution close to the pK<sub>a</sub> of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. The

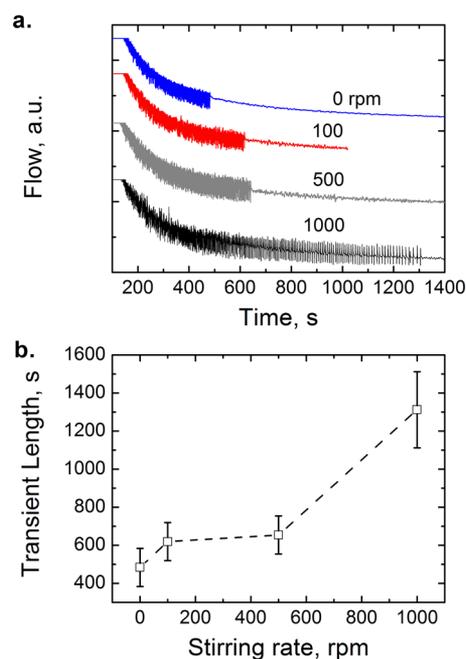


**Figure 3.** Dependence of  $\text{H}_2$  flow dynamics upon the initial pH of  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  buffer. Experiments were performed at  $30\text{ }^\circ\text{C}$  with 1 M buffer solutions of  $\text{NaH}_2\text{PO}_4$  and 2.6 M of  $\text{NaBH}_4$ . The stirring rate is 1000 rpm. The initial pH of the solution was varied in the interval [5.00, 7.00], and the resulting dynamics are compared over an arbitrary flow scale in panel a. Typical excursions of the bursts range from 5 to 20 sccm. Panel b shows a characterization of the oscillatory transient length as a function of the buffer pH. Each point is an average value of three experiments.

system is, in fact, kept under quasi-stationary weakly alkaline conditions in which oscillations appear favored for a longer period. Beyond this pH value, we obtained mainly erratic and scarcely reproducible evolutions of the gas. Finally, note that this buffering of the reactive mixture suppresses sinusoidal-type oscillations.

The effective importance of the pH buffering strength in terms of stabilization of the oscillatory regime was also confirmed by comparing experiments carried out with a decreasing concentration the buffer solution. We observed that less concentrated buffers induce shorter oscillatory transients characterized by a smaller amplitude, and, in the limited case of pure water (in other words, with a solution with a null buffering strength), the occurrence of these bursting regimes is statistically irrelevant.

**Influence of the Stirring.** A further experimental factor that can affect the oscillatory gas out-flow dynamics when the reaction is carried out with  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  buffers is the stirring rate of the reactive mixture. Similarly to the initial pH, this parameter influences both the length and the oscillation frequency of the bursting transient. In Figure 4a we compare the reaction dynamics for increasing values of the stirring rate. Experiments were performed at  $30\text{ }^\circ\text{C}$  with 1.5 g of  $\text{NaBH}_4$  and 15 mL of a buffer solution 1 M of  $\text{NaH}_2\text{PO}_4$  (i.e.,  $c_{\text{NaBH}_4} = 2.6\text{ M}$ , initial pH 7.00). An increase in the oscillatory transient length (see Figure 4b) is observed while augmenting the stirring rate.

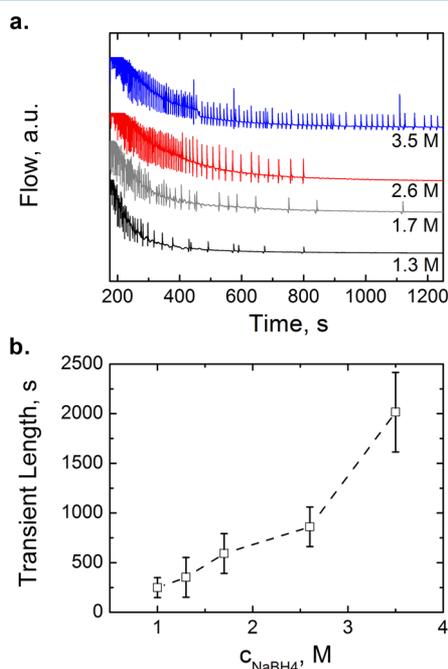


**Figure 4.** Dependence of  $\text{H}_2$  flow dynamics on the stirring rate. Experiments were performed at  $30\text{ }^\circ\text{C}$  with buffer solutions in concentration 1 M of  $\text{NaH}_2\text{PO}_4$  and 2.6 M of  $\text{NaBH}_4$ , pH 7.00. The stirring rate was varied between 0 and 1000 rpm and the resulting dynamics are compared over an arbitrary flow scale in panel a. Panel b shows a characterization of the oscillatory transient length as a function of the stirring rate. Each point is an average value of three experiments.

Indeed, the dependence of the dynamics upon the stirring rate should not be confused with the critical effect that stirring exerts in gas evolution oscillators (bubblelators).<sup>18,19</sup> In bubblelators an improper stirring, either too fast or too slow, kills the onset and the persistence of the oscillatory development of bubbles. As we did in our previous investigation,<sup>17</sup> we checked this fact by also following the system dynamics when a glass powder is introduced in the reactive mixture. In a real bubblelator the presence of such heterogeneities creates nucleation points, thus avoiding the possibility for gas supersaturation in the solution, which is at the basis of the oscillatory mechanism. In our system we could not reveal any difference between these dynamics with those characterizing the glass-powder-free system. In the context of  $\text{NaBH}_4$  hydrolysis, stirring has no critical effect on the onset of the oscillatory instability but it rather promotes and homogenizes the gas delivery from the reactive mixture.

**Influence of the  $\text{NaBH}_4$  Initial Concentration.** A typical feature of chemical oscillators is the dependence upon the concentration of the initial reactants. In batch chemical oscillators, the main reactant concentration acts as a *pseudoparameter* able to control the properties of chemical oscillations during the reaction development, even affecting the possibility for the oscillatory instability to occur.<sup>22–26</sup> In the system under analysis, we explored the influence of the initial reactants by systematically changing the amount of  $\text{NaBH}_4$  in a fixed volume (15 mL) of 1 M  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  buffer solutions. Experiments were performed at  $30\text{ }^\circ\text{C}$ , with a stirring rate equal to 1000 rpm and initial pH 6.00. The flow dynamics presents a clear sensitivity to the initial concentration of  $\text{NaBH}_4$ . We also observe that oscillation frequency decreases when lowering  $\text{NaBH}_4$  initial concentration, and, as expected,

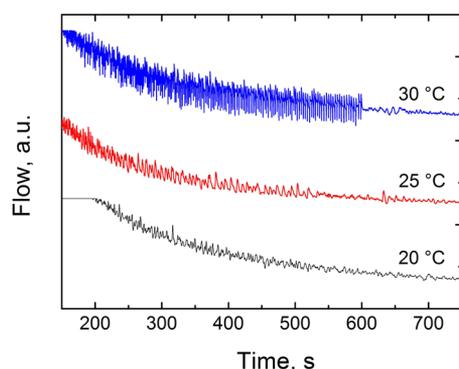
the bursting oscillations persist longer while increasing  $\text{NaBH}_4$ . This feature is shown in Figure 5a, where we report the



**Figure 5.** Dependence of  $\text{H}_2$  flow dynamics upon the initial concentration of  $\text{NaBH}_4$ . Experiments were performed at  $30\text{ }^\circ\text{C}$  with buffer solutions 1 M of  $\text{NaH}_2\text{PO}_4$  and 1.3, 1.7, 2.6, and 3.5 M of  $\text{NaBH}_4$ . The stirring rate was 1000 rpm and the initial pH 6.00. The resulting dynamics are compared over an arbitrary flow scale in panel a, and the related transient lengths are characterized in panel b. Each point in panel b is an average value of three experiments.

temporal evolution of the gas out-flow for different concentrations,  $c_{\text{NaBH}_4}$  of the  $\text{NaBH}_4$  solutions, and the related characterization is illustrated in Figure 5b. No oscillations can be found below the critical threshold  $c_{\text{NaBH}_4} < 0.9\text{ M}$ .

**Influence of the Bath Temperature.** The temperature at which the reaction is carried out also plays a crucial role in the onset of the oscillatory instability. In Figure 6 we show the  $\text{H}_2$  out-flow dynamics obtained from experiments performed at different temperature with 1.5 g of  $\text{NaBH}_4$  and 15 mL of a



**Figure 6.** Dependence of  $\text{H}_2$  flow dynamics upon the working temperature. Experiments were performed with 1.5 g of  $\text{NaBH}_4$  and 15 mL of buffer solution 1 M of  $\text{NaH}_2\text{PO}_4$  (i.e.,  $c_{\text{NaBH}_4} = 2.6\text{ M}$ , pH 6.00, and the stirring rate was 1000 rpm). Bursting-type oscillatory transients appear in a reproducible way beyond  $30 \pm 0.5\text{ }^\circ\text{C}$ .

buffer solution 1 M of  $\text{NaH}_2\text{PO}_4$  (i.e.,  $c_{\text{NaBH}_4} = 2.6\text{ M}$ , initial pH 6.00 and a stirring rate equal to 1000 rpm). Bursting dynamics occur when the temperature is larger than  $30\text{ }^\circ\text{C} \pm 0.5$ , while erratic behaviors can be found if the working temperature is below this threshold. As the working temperature is led beyond  $30\text{ }^\circ\text{C}$ , the flow baseline is shifted to higher values, and the oscillation frequency and amplitude also increase. By contrast, the length of the transient shrinks, indicating that the amount of gas delivered in this initial reaction phase tends to be conserved.

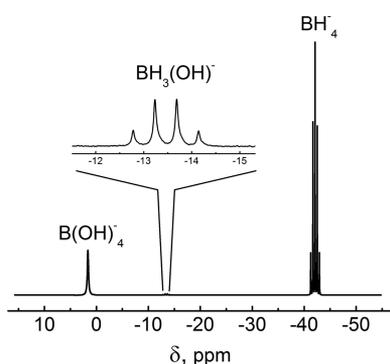
A further indirect evidence of the thermal influence on the system dynamics has also been pointed out by changing the material of the reactor. In check experiments, we compared the typical dynamics resulting from  $\text{NaBH}_4$  hydrolysis conducted under analogous conditions but in a reactor made of quartz and in another one made of plexiglass. The oscillatory transient was found to be shorter for the experiments in the quartz reactor, as it is able to dissipate faster the heat developed during the exothermic hydrolysis process.

## ■ A POSSIBLE MECHANISM FOR OSCILLATIONS

**Permissible Species.** In the light of the experimental evidence found in this and previous studies,<sup>17</sup> gas out-flow oscillations in  $\text{NaBH}_4$  hydrolysis appear coupled to an ‘oscillating chemical core’ in the homogeneous phase of the reactive mixture. If we stick to the reaction schemes 2–4, the set of species that can be involved in such a nonlinear mechanism in  $\text{NaBH}_4$  hydrolysis is restricted to (i) the initial reactants,  $\text{NaBH}_4$  and water (protons and hydroxides), (ii) the reaction products, metaborates and  $\text{H}_2$ , and (iii) the intermediates,  $\text{BH}_3$  and  $\text{BH}_3^-$ . In batch chemical oscillators the initial reactants and the ultimate products can follow stepwise concentration evolutions over a decreasing or an increasing monotonic trend, respectively. Indeed, initial reactants represent the engine of the oscillatory mechanism, while only reaction intermediates can effectively take part in the oscillatory mechanism. The smooth and monotonous pH variation in the course of the reaction excludes the fact that  $\text{H}^+$  or  $\text{OH}^-$  are involved in the oscillatory dynamics.  $\text{BH}_3^-$  is a fast transient species, and only  $\text{BH}_3$  features a reliable oscillatory chemical variable.

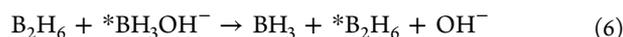
However, an oscillatory instability implies the presence of at least two oscillatory intermediates. Recent  $^{11}\text{B}$  NMR inspections on the  $\text{NaBH}_4$  hydrolysis mixture have shown that the species  $\text{BH}_3\text{OH}^-$  also forms during the hydrolysis reaction. In this study we have confirmed this result and in Figure 7 we report the proton-coupled  $^{11}\text{B}$  NMR spectrum. The main signals, the singlet at 1.6 ppm and the quintet at  $-42.1\text{ ppm}$ , correspond to  $\text{NaB}(\text{OH})_4$  and  $\text{BH}_4^-$ , respectively. Perusal of Figure 7 at  $-13.5\text{ ppm}$  allows us to appreciate a small quartet over the noisy baseline of the spectrum. This signal is related to the species  $\text{BH}_3\text{OH}^-$ , while no other hydroxyborate can be detected.  $\text{BH}_3\text{OH}^-$  can feature a second candidate as an oscillating intermediate species.

**Implemented Kinetic Scheme.** According to the general theory on chemical oscillations,<sup>22,27,28</sup> to meet conditions for oscillations in homogeneous phase, one nonlinear step such as an autocatalysis or an isomorphic process must be at play. However, kinetic model 2–4 consists of a set of pseudo-first-order elementary steps that cannot explain the emergence of oscillatory instabilities. Following the kinetic scheme proposed by Lefever et al.<sup>29</sup> to interpret and decompose a third-molecular

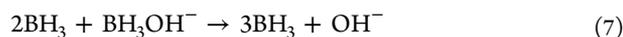


**Figure 7.** Proton-coupled  $^{11}\text{B}$  NMR spectrum of the aqueous  $\text{NaBH}_4$ . The singlet at 1.6 ppm is associated with  $\text{NaB}(\text{OH})_4$ , while the quintet at  $-42.1$  ppm refers to  $\text{BH}_4^-$ . The  $J_{\text{BH}}$  spin–spin coupling constant for  $\text{BH}_4^-$  equals 80.6 Hz, in agreement with previous work.<sup>16</sup> The small signal at  $-13.5$  ppm ( $J_{\text{BH}}$  spin–spin coupling constant equal to 87.5 Hz) can be assigned to the intermediate  $\text{BH}_3\text{OH}^-$ .

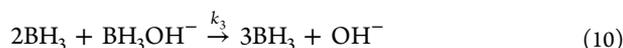
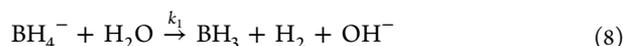
step, we hypothesize a possible cubic autocatalysis in  $\text{NaBH}_4$  hydrolysis by coupling the equilibrium between  $\text{BH}_3$  and  $\text{B}_2\text{H}_6$  with an isotopic exchange mechanism between the latter and  $\text{BH}_3\text{OH}^-$



Assuming that [step 5](#) develops with a significantly different temporal scale as compared to [step 6](#) and is quickly reaching a stationary state, we can apply the standard adiabatic approximation,<sup>29</sup>  $d[\text{B}_2\text{H}_6]/dt = 0$ , and rewrite the global step as



On the basis of these considerations, we propose here an implementation of kinetic [model 2–4](#) by introducing the globally autocatalytic [step 7](#)



where  $P$  represents the final product (namely, boric acid or sodium metaborate or tetrahydroborate depending on the pH; this does not affect the system dynamics). Here  $\text{BH}_4^-$  maintains the system under far-from-equilibrium conditions, and, assuming a stationary description of the oscillatory regime (i.e., with the reactant slowly depleted), its concentration can be assumed as a constant. In the same way,  $[\text{OH}^-]$  is taken as a constant because the experiments suggest that oscillatory dynamics occur in an optimal, slightly alkaline pH range. The steps describing the formation and the consumption of the fast chemical variable  $\text{BH}_5$  have been included in [reaction 8](#). The set of kinetic equations corresponding to the new kinetic mechanism now reads

$$\frac{d[\text{BH}_3]}{dt} = k_1[\text{BH}_4^-] - (k_2 + k_4)[\text{BH}_3] + k_3[\text{BH}_3]^2[\text{BH}_3(\text{OH})^-] \quad (12)$$

$$\frac{d[\text{BH}_3(\text{OH})^-]}{dt} = k_2[\text{BH}_3] - k_3[\text{BH}_3]^2[\text{BH}_3(\text{OH})^-] \quad (13)$$

$$\frac{d[\text{H}_2]}{dt} = k_1[\text{BH}_4^-] + 3k_4[\text{BH}_3] \quad (14)$$

Kinetic [eq 14](#), describing  $\text{H}_2$  production, is decoupled to the first two functions, and thus the system dynamics can be reduced to [eqs 12 and 13](#). Within this description, when the condition for the Hopf instability

$$[\text{OH}]_c^- > (k_1^2 k_3 [\text{BH}_4^-]^2 + k_4^3) / (k_2 k_4^2) \quad (15)$$

is satisfied,<sup>22,29</sup> chemical variables  $[\text{BH}_3]$  and  $[\text{BH}_3\text{OH}^-]$  can oscillate. The [subsystem 12 and 13](#) acts as a minimal oscillator, which provides the driving force for hydrogen flow oscillations and represents here a general proof of concept that sodium borohydride hydrolysis can undergo an oscillatory instability. In this stage the model cannot be asked for a quantitative agreement with the experimental observable, which is the out-flow of gaseous  $\text{H}_2$ . Indeed, the kinetic constants are unknown and the kinetics ruling the gas delivery from the solution may be a complicated function of both the stirring rate and the temperature. In this sense a direct comparison between experimental dynamics and simulations of [eqs 12 and 13](#) can be misleading and is not included in this paper. Nevertheless, this kinetic scheme represents a solid basis able to explain important features of the system observed in the experiments. It can predict, for instance, a lower pH threshold for the emergence of an oscillatory behavior, while an upper pH threshold is vice versa dictated by the fact that the reaction becomes inhibited when the pH approaches 10.5. In the weakly alkaline pH regime the oscillatory species  $\text{BH}_3\text{OH}^-$  can form, and a minimal amount of this intermediate appears crucial to initiate oscillations. Also, from the analysis of kinetic [eqs 12 and 13](#) one can expect<sup>22</sup> that the oscillation frequency augments with the initial concentration of the main reactant, and this feature favorably compares with what observed in the experiments.

## CONCLUDING DISCUSSION

The  $\text{NaBH}_4$  hydrolysis is a promising process for the portable generation of a green and alternative fuel, molecular hydrogen. To open such a perspective, a robust control of the kinetics of gas formation is needed. In this and in a previous paper<sup>17</sup> we have shown that this reaction may present deterministic nonlinear behaviors in a wide range of experimental conditions, and two typical oscillatory scenarios in the delivery of gaseous molecular hydrogen have been identified. Despite the impact that such oscillatory dynamics may present in applicative terms, a complete kinetic picture to explain these phenomena is still missing. Here we have focused on bursting-type dynamics, which were previously found difficult to be isolated. We have stabilized in a reproducible way the conditions for this oscillatory instability by performing experiments with highly concentrated  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$  pH buffers, which allowed us to increase the buffering strength. Bursting oscillatory transients were critically sensitive upon the initial pH, the buffering strength, and the working temperature. In particular, vigorous and high-frequency oscillations appear and damp down quite fast under weakly acidic conditions. Conversely, bursting transients are stabilized (transient oscillations persist longer) within a slightly alkaline pH range around 7.2, where the buffering strength is maximal and the reaction maintains

quasi-stationary conditions for a longer period. The system undergoes bursting-type oscillations beyond the threshold temperature  $30\text{ }^{\circ}\text{C} \pm 0.5$ , and long-lasting oscillations are also favored by high stirring rates.

On the basis of the experimental dependences and  $^{11}\text{B}$  NMR analytical investigations of the reactive mixture, we have proposed a possible kinetic scheme consistent with the mechanism given in the literature for this reaction. Specifically, we have implemented an autocatalytic step involving intermediates  $\text{BH}_3$  and  $\text{BH}_3\text{OH}^-$ , which may explain the onset of oscillations. The resulting kinetic scheme, isomorphic with another prototypical model for oscillations, the Brusselator,<sup>29</sup> captures the need for slightly alkaline conditions, in which the critical intermediate  $\text{BH}_3\text{OH}^-$  forms. Our model also substantiates the importance of the buffering strength to maintain optimal chemical conditions for the oscillatory instability and to avoid a fast evolution toward too basic pH values where the reaction is inhibited. The increase in the oscillation frequency as a function of the initial reactant concentration characterizing this model also compares favorably with experiments. Within our description,  $\text{H}_2$  does not play any active role in the oscillating mechanism but is coupled and driven by the chemical *oscillophor* in the reactive solution. Further studies to support this implemented model are in progress via a systematic characterization of the essential kinetic steps, with a particular focus on the autocatalytic one. To this end, other convenient precursors of the intermediates of interest  $\text{BH}_3\text{OH}^-$ , such as  $\text{NH}_3\text{BH}_3$ , are under consideration. Finally, this study also features an important contribution in the context of nonlinear chemistry as  $\text{NaBH}_4$  hydrolysis represents an original chemical oscillator that challenges us with a completely new chemistry (based on boron compounds) with respect to known oscillators.

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### Notes

The authors declare no competing financial interest.

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