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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 behaviours of H_2 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 non-desirable fluctuations in the production of molecular hydrogen. Despite the potential of $NaBH_4$ 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 $NaBH_4$ 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 hypothesise 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 many scientific evidence indicate that the exponential use of fossil resources increases CO_2 and other greenhouse gases in the atmosphere, thus provoking an increasing global warming and climate changes.[1] 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 features 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 by-product. 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_2 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.[2,3] Among borohydride systems, sodium borohydride, $NaBH_4$, is viewed with interest because of its considerable hydrogen gravimetric capacity, high stability in air, and low price. Hydrogen generation *via* $NaBH_4$ follows two main routes: thermolysis and hydrolysis. The latter, globally described by the reaction

$$\mathrm{NaBH_4(aq)} + 4\mathrm{H_2O} \longrightarrow \mathrm{NaB(OH)_4(aq)} + 4\mathrm{H_2(g)} + heat\,, \tag{1}$$

is a spontaneous and exothermic reaction that works in mild conditions.[4] This process yields environmentally safe by–products (in particular borates that can be re-cycled) and features a convenient strategy for *in-situ* generation of highly pure hydrogen that can used as a green fuel.[5] 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 $NaBH_4$ and of hydrated sodium metaborate ($NaBO_2$)[6] 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 in controlled conditions. A further problem is represented by nonlinear phenomena that can occur during the development of the reaction.[7,8] Though never instigated in depth, long-lasting periodic and more complicated oscillations have been shown in previous works where $NaBH_4$ hydrolysis is performed in open conditions and in the presence of homogeneous catalysts such as nickel complexes.[9–11] Though many efforts have been devoted to enlighten the mechanism of the reaction,[12–16] important kinetic details that can explain the onset of oscillatory behaviours are still scarcely understood.

Recently we have systematically undertaken a kinetic study of $NaBH_4$ hydrolysis and shown that the non-catalysed hydrolysis can also exhibit oscillatory transients in the hydrogen generation.

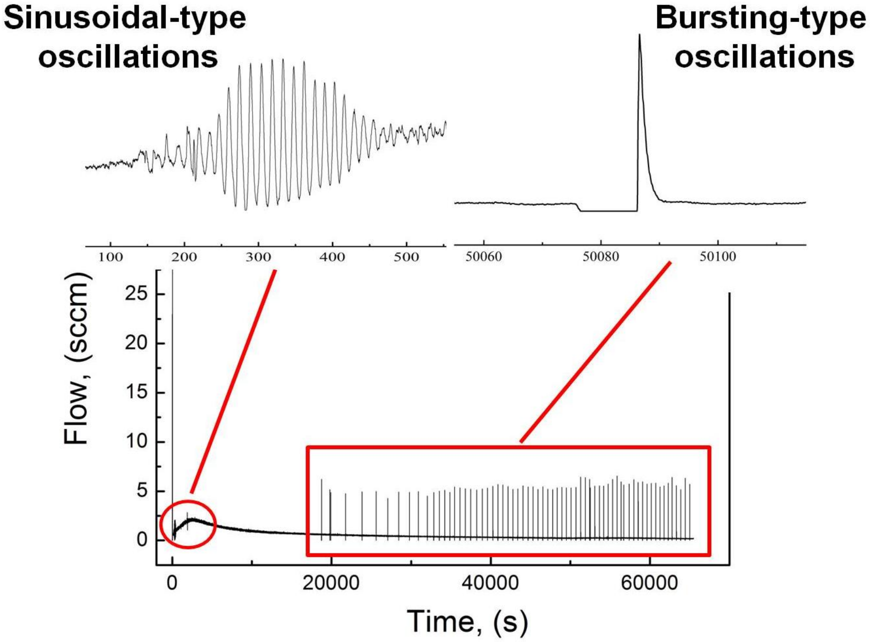

Figure 1: Example of gaseous H_2 out-flow in the non-catalysed $NaBH_4$ hydrolysis carried out with 1.5 g of $NaBH_4$ and 15 ml of distilled water (i.e. c_{NaBH_4}=2.6 M) at 30 °C. The dynamics can show two typical oscillatory scenarios: a sinusoidal-type transient and a bursting-type regime. Flow is given in standard cubic centimeters per minute (sccm).

Fig. 1 illustrates a time series of the gas delivered during $NaBH_4$ 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 around 10 oscillations with a characteristic period of 18 $\pm$2 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 of 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 in the reaction conditions considered).

In a previous study[17] we focused on the sinusoidal-type transient. Thanks to a series of *ad-hoc* experiments we gave evidence that this oscillatory behaviour is not the result of any instrumental artifices or stochastic fluctuations but it rather features a deterministic phenomenon which 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)[18,19] or by a thermo-kinetic interplay. Also, we could infer that gas flow oscillations are most probably driven by a chemical "oscillophor" in the reactive mixture.[20,21]

While sinusoidal-type transients were controlled and characterized at a large extent, bursting-like scenarios were found 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. Based on analytical investigations, we finally propose a minimal mechanism which may explain the onset of oscillatory instabilities in this system.

Experimental

Experiments were carried out in batch conditions in a 25 ml quartz (or plexiglass) cylindrical reactor (see a schematic of the setup in Fig. 1). We used different quantities of $NaBH_4$ (98% Sigma-Aldrich, powder) in a fixed volume (15 ml) of fresh prepared NaH_2PO_4/Na_2HPO_4 pH buffers. Buffer solutions were prepared by using 1.00 M solutions of NaH_2PO_4 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_2PO_4 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. $NaBH_4$ was kept under argon atmosphere (specifically in a glove-box) in order to avoid the aging of the salt due to hydration.

$NaBH_4$ fine powder was loaded into the reactor under 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 $NaBH_4$ 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 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.

^{11}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_2O and 1 wt% D_2O) and 0.5 g of $NaBH_4$. The percent of deuterated water should be limited since it enhances and modify 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.

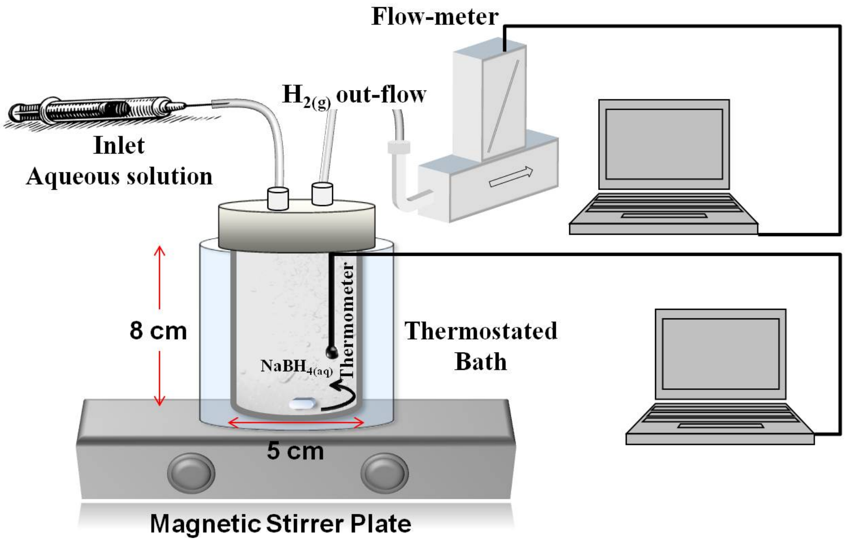

Figure 2: Sketch of the experimental setup.

Experimental results

Influence of the pH

$NaBH_4$ hydrolysis and the related production of gaseous molecular hydrogen are strictly sensitive to the solution pH. To be more precise, the process is favoured in 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 9.00–10.5, where the pH variation is much slower. The dependence of H_2 generation on the pH in borohydrides hydrolysis is embedded in the classical kinetic scheme used to describe the reaction:[12–14]

$$
\begin{aligned}
BH_4^- + H^+ &\xrightarrow{k_1} BH_5 \,, && (2)\\
BH_5 &\xrightarrow{k_2} BH_3 + H_2 \,, && (3)\\
BH_3 + 3H_2O &\xrightarrow{k_3} H_3BO_3 + 3H_2 \,, && (4)
\end{aligned}
$$

where H_3BO_3 progressively converts into sodium metaborate and tetrahydroborate while pH increases. It can be observed that H^+ fuels the conversion of $NaBH_4$ 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. $MgCO_3$ is in fact present as an anti-caking agent in the $NaBH_4$ powder at hands (0.4 - 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 behaviour 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_2PO_4/Na_2HPO_4 system. This pH buffer allows us to work with more acidic initial pH values, typically in the range [5.00-8.00) (the pK_a of $H_2PO_4^-$ is around 7.2). Furthermore, as compared to our previous exploration, we use more concentrated buffer solutions ($\sim$ 1 M) to increase the pH buffering strength of the reactive solution. The solubility of $NaBH_4$ is not significantly affected by this fact.

In Fig. 3.a we resume the typical dynamics obtained when the reaction is performed with 1.5 g of $NaBH_4$ and 15 ml of 1 M NaH_2PO_4/Na_2HPO_4 buffer solution (i.e. c_{NaBH_4}=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. In 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. Though the time series is strongly non-stationary (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 analysed in Fig. 3.b, can be ascribed to the maximal buffering strength of the solution close to the pK_a of $H_2PO_4^-$. The system is, in fact, kept in quasi-stationary weakly alkaline conditions in which oscillations appear favoured 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 limit 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 NaH_2PO_4/Na_2HPO_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 Fig. 4.a we compare the reaction dynamics for increasing values of the stirring rate. Experiments were performed at 30 °C with 1.5 g of $NaBH_4$ and 15 ml of a buffer solution 1 M of NaH_2PO_4 (i.e. c_{NaBH_4}=2.6 M, initial pH = 7.00). An increase of the oscillatory transient length (see Fig. 4.b) is observed while augmenting the stirring rate.

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).[18,19] 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,[17] 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 $NaBH_4$ hydrolysis, stirring has no critical effect on the onset of the oscillatory instability but it rather promotes and homogenize the gas delivery from the reactive mixture.

Influence of the $NaBH_4$ 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 *pseudo-parameter* able to control the properties of chemical oscillations during the reaction development, even affecting the possibility for the oscillatory instability to occur.[22–26] In the system under analysis, we explored the influence of the initial reactants by changing systematically the amount of $NaBH_4$ in a fixed volume (15 ml) of 1 M NaH_2PO_4/Na_2HPO_4 buffer solutions. Experiments were performed at 30 °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 $NaBH_4$. We also observe that oscillation frequency decreases when lowering $NaBH_4$ initial concentration and, as expected, the bursting oscillations persist longer while increasing $NaBH_4$. This feature is shown in Fig. 5.a where we report the temporal evolution of the gas out-flow for different concentrations, c_{NaBH_4}, of the $NaBH_4$ solutions and the related characterization is illustrated in Fig. 5.b. No oscillations can be found below the critical threshold $c_{NaBH_4} < 0.9$ 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 Fig. 6 we show the H_2 out-flow dynamics obtained from experiments performed at different temperature with 1.5 g of $NaBH_4$ and 15 ml of a buffer solution 1 M of NaH_2PO_4 (i.e. c_{NaBH_4}=2.6 M, initial pH=6.00 and a stirring rate equal to 1000 rpm). Bursting dynamics occur when the temperature is larger than 30 °C ± 0.5, while erratic behaviours can be found if the working temperature is below this threshold. As the working temperature is led beyond 30 °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 been also pointed out by changing the material of the reactor. In check experiments, we compared the typical dynamics resulting from $NaBH_4$ hydrolysis conducted in 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,[17] gas out-flow oscillations in $NaBH_4$ hydrolysis appear coupled to an 'oscillating chemical core' in the homogeneous phase of the reactive mixture. If we stick to the reaction scheme (2–4), the set of species that can be involved in such a nonlinear mechanism in $NaBH_4$ hydrolysis is restricted to (*i*) the initial reactants, $NaBH_4$ and water (protons and hydroxides), (*ii*) the reaction products, metaborates and H_2, and (*iii*) the intermediates BH_3 and BH_5. In batch chemical oscillators the initial reactants and the ultimate products can follow step-wise 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 take effectively part to the oscillatory mechanism. The smooth and monotonous pH variation in the course of the reaction excludes that H^+ or OH^- are involved in the oscillatory dynamics. BH_5 is a fast transient species and only BH_3 features a reliable oscillatory chemical variable.

However an oscillatory instability implies the presence of, at least, two oscillatory intermediates. Recent ^{11}B NMR inspections on the $NaBH_4$ hydrolysis mixture have shown that the species BH_3OH^- also forms during the hydrolysis reaction. In this study we have confirmed this result and in Fig. 7 we report the proton coupled ^{11}B NMR spectrum. The main signals, the singlet at 1.6 ppm and the quintet at -42.1 ppm, correspond to $NaB(OH)_4$ and BH_4^-, respectively. Perusal of Fig. 7 at -13.5 ppm allows us to appreciate a small quartet over the noisy base line of the spectrum. This signal is related to the species BH_3OH^-, while no other hydroxyborate can be detected. BH_3OH^- can feature a second candidate as an oscillating intermediate species.

Implemented kinetic scheme

According to the general theory on chemical oscillations,[22,27,28] in order 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.[29] to interpret and decompose a third-molecular step, we hypothesise a possible cubic autocatalysis in $NaBH_4$ hydrolysis by coupling the equilibrium between BH_3 and B_2H_6 with an isotopic exchange mechanism between the latter and BH_3OH^-:

$$2BH_3 \rightleftharpoons B_2H_6 \tag{5}$$

$$B_2H_6 + {}^*BH_3OH^- \rightarrow BH_3 + {}^*B_2H_6 + OH^- \tag{6}$$

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,[29] $d[B_2H_6]/dt = 0$, and re–write the global step as

$$2BH_3 + BH_3OH^- \rightarrow 3BH_3 + OH^- \tag{7}$$

On the basis of these considerations, we propose here an implementation of kinetic model (2–4) by introducing the globally auto–catalytic step (7):

$$BH_4^- + H_2O \xrightarrow{k_1} BH_3 + H_2 + OH^- \tag{8}$$

$$BH_3 + OH^- \xrightarrow{k_2} BH_3OH^- \tag{9}$$

$$2BH_3 + BH_3OH^- \xrightarrow{k_3} 3BH_3 + OH^- \tag{10}$$

$$BH_3 + 3H_2O \xrightarrow{k_4} P + 3H_2\,. \tag{11}$$

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 BH_4^- maintains the system in 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, $[OH^-]$ is taken as a constant, since 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 BH_5 have been included in reaction (8). The set of kinetic equations corresponding to the new kinetic mechanism now reads

$$\begin{aligned}
\frac{d[BH_3]}{dt} &= k_1[BH_4^-] - (k_2 + k_4)[BH_3] \\
&\quad + k_3[BH_3]^2[BH_3(OH)^-] \qquad (12) \\
\frac{d[BH_3(OH)^-]}{dt} &= k_2[BH_3] - k_3[BH_3]^2[BH_3(OH)^-] \qquad (13) \\
\frac{d[H_2]}{dt} &= k_1[BH_4^-] + 3k_4[BH_3] \qquad (14)
\end{aligned}$$

Kinetic equation (14), describing H_2 production, is decoupled to the first two functions and, thus, the system dynamics can be reduced to equation set (12–13). Within this description, when the condition for the Hopf instability,

$$[OH]_c^- > (k_1^2 k_3 [BH_4^-]^2 + k_4^3)/(k_2 k_4^2), \qquad (15)$$

is satisfied,[22,29] chemical variables $[BH_3]$ and $[BH_3OH^-]$ can oscillate. The sub-system (12–13) acts as a minimal oscillophor 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. At this stage the model cannot be asked for a quantitative agreement with the experimental observable which is the out-flow of gaseous 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. (12–13) 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 behaviour 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 BH_3OH^- can form and a minimal amount of this intermediate appears crucial to initiate oscillations. Also, from the analysis of kinetic equations (12–13) one can expect[22] that the oscillation frequency augments with the initial concentration of the main reactant and this feature favourably compares with what observed in the experiments.

Concluding discussion

The $NaBH_4$ 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[17] we have shown that this reaction may presents deterministic nonlinear behaviours 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 NaH_2PO_4/Na_2HPO_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 in 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 °C

±0.5 and long-lasting oscillations are also favoured by high stirring rates.

Based on the experimental dependences and ^{11}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 BH_3 and BH_3OH^-, which may explain the onset of oscillations. The resulting kinetic scheme, isomorphic with another prototypical model for oscillations, the Brusselator,[29] captures the need for slightly alkaline conditions, in which the critical intermediate BH_3OH^- forms. Our model also substantiate the importance of the buffering strength to maintain optimal chemical conditions for the oscillatory instability and to avoid a fast evolution towards too basic pH values where the reaction is inhibited. The increase of the oscillation frequency as a function of the initial reactant concentration characterizing this model also compares favourably with experiments. Within our description, 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 BH_3OH^-, such as NH_3BH_3, are under consideration. Finally, this study also features an important contribution in the context of nonlinear chemistry as $NaBH_4$ 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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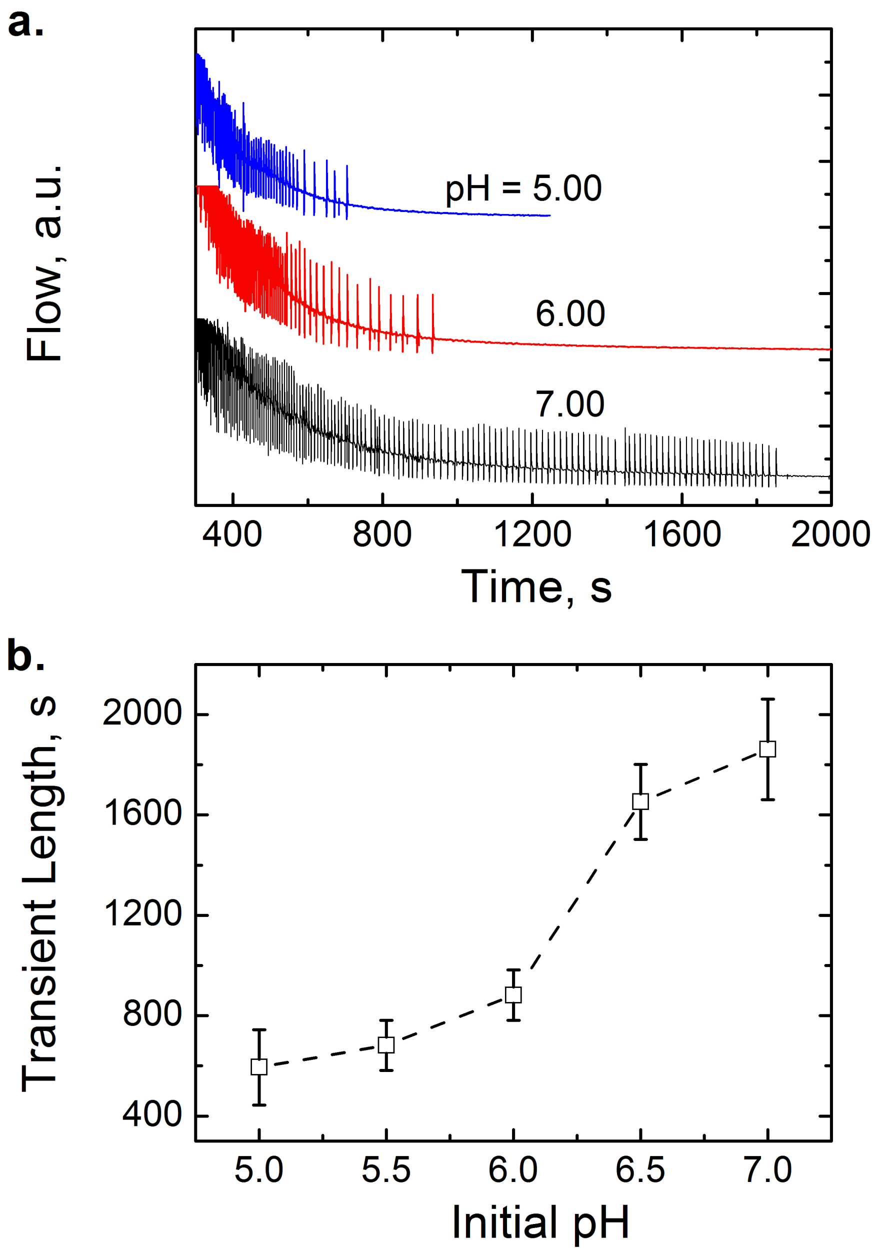

Figure 3: Dependence of H_2 flow dynamics upon the initial pH of NaH_2PO_4/Na_2HPO_4 buffer. Experiments were performed at 30 °C with 1 M buffer solutions of NaH_2PO_4 and 2.6 M of $NaBH_4$. The stirring rate is 1000 rpm. The initial pH of the solution was varied in the interval [5.00, 7.00] and the resulting dynamics are compared over an arbitrary flow scale in panel (a). Typical excursions of the bursts range in [5-20] 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 3 experiments.

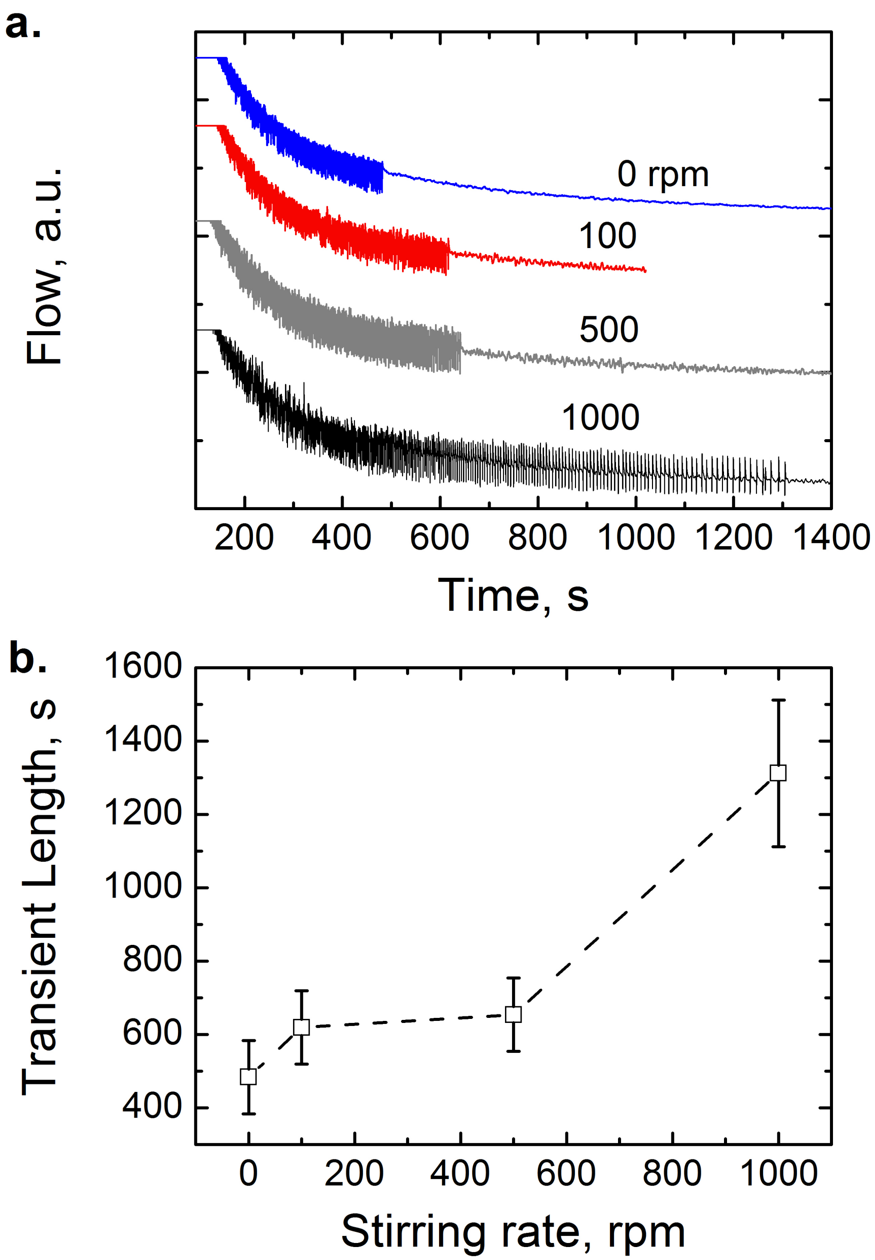

Figure 4: Dependence of H_2 flow dynamics on the stirring rate. Experiments were performed at 30 °C with buffer solutions in concentration 1 M of NaH_2PO_4 and 2.6 M of $NaBH_4$, pH = 7.00. The stirring rate was varied between 0 and 1000 rpm and the resulting dynamics are compared over an arbitrary flow 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 3 experiments.

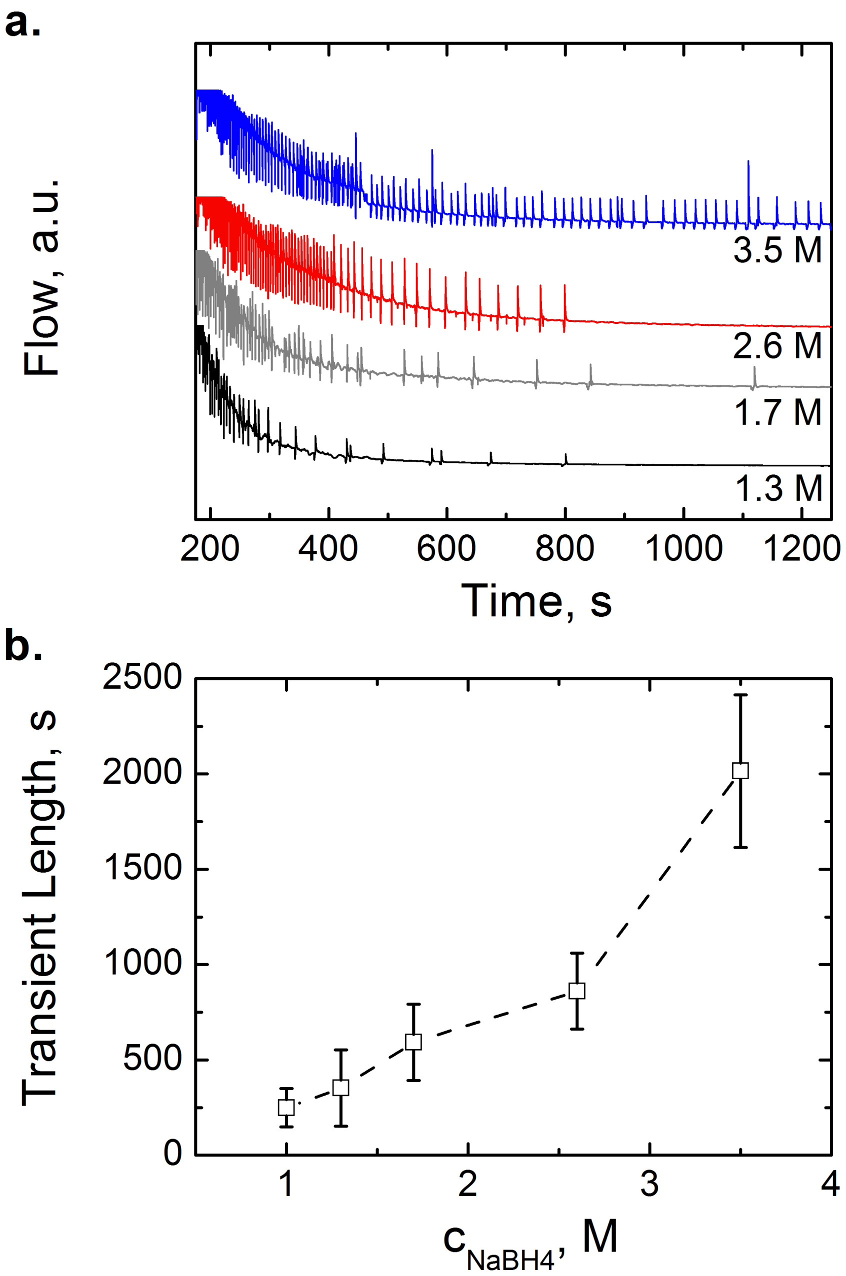

Figure 5: Dependence of H_2 flow dynamics upon the initial concentration of $NaBH_4$. Experiments were performed at 30 °C with buffer solutions 1 M of NaH_2PO_4 and 1.3 M, 1.7 M, 2.6 M and 3.5 M of $NaBH_4$. The stirring rate was 1000 rpm and the initial pH=6.00. The resulting dynamics are compared over an arbitrary flow scale in panel (a) and the related transient lengths are characterized in panel (b). Each point in (b) is an average value of 3 experiments.

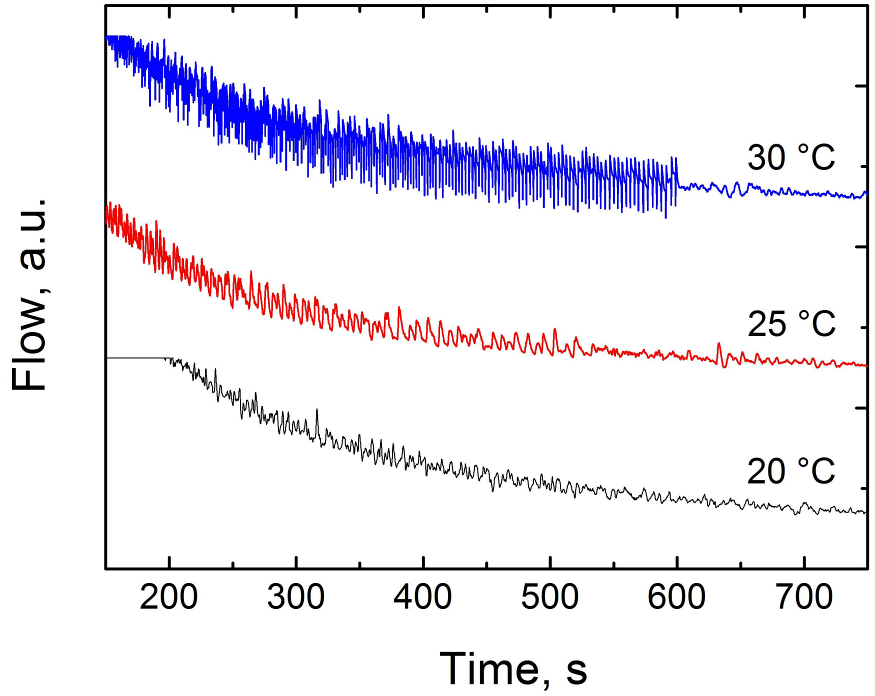

Figure 6: Dependence of H_2 flow dynamics upon the working temperature. Experiments were performed with 1.5 g of $NaBH_4$ and 15 ml of buffer solution 1 M of NaH_2PO_4 (i.e. c_{NaBH_4}=2.6 M, pH=6.00 and the stirring rate was 1000 rpm). Bursting-type oscillatory transients appear in a reproducible way beyond 30 ±0.5 °C.

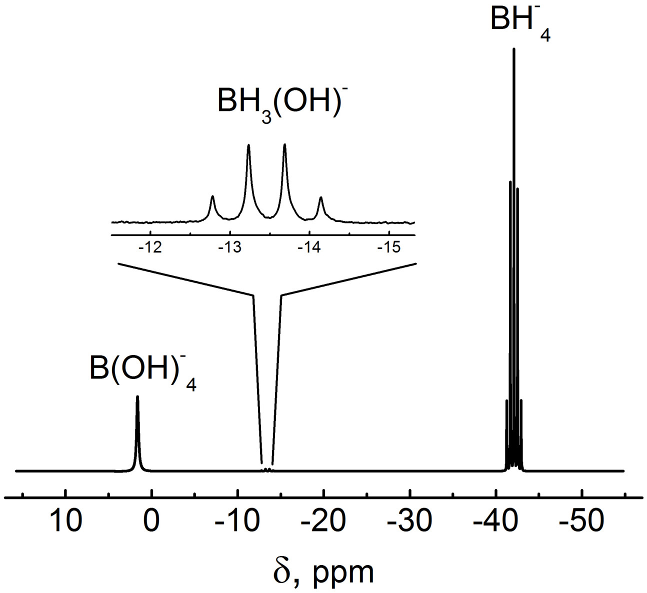

Figure 7: Proton coupled ^{11}B NMR spectrum of the aqueous NaBH$_4$. The singlet at 1.6 ppm is associated to NaB(OH)$_4$ while the quintet at -42.1 ppm refers to BH$_4^-$. The J_{BH} spin-spin coupling constant for BH$_4^-$ equals 80.6 Hz, in agreement with previous work.[16] The small signal at -13.5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

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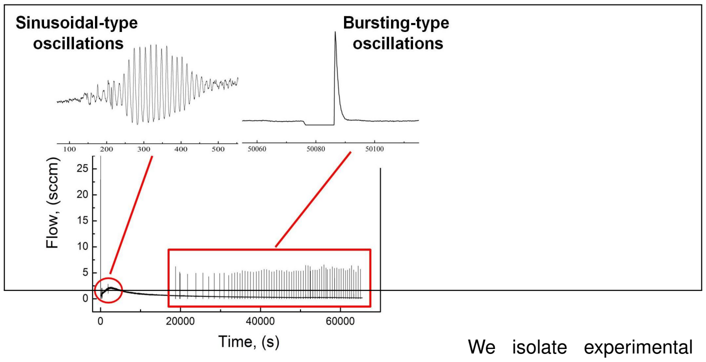
Graphical TOC Entry



We isolate experimental conditions for the onset of bursting-type oscillations in the out-flow of gaseous H_2 from $NaBH_4$ hydrolysis. A minimal kinetic model for justifying the onset of an oscillatory instability in this system is also presented.